



Utilization of Alternate Propellants to Reduce Stratospheric Ozone Depletion

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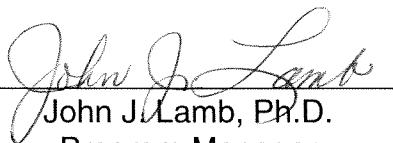
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1.0 Overview

There is continuing concern about the depletion of the ozone layer. Recently it has been determined that effluents from rockets exhausts contain chemical species that can be classified as Potentially Ozone Reactive Chemicals (PORCs). Calculations on the destruction of ozone layer suggest that that rockets contribute about ~1% to the overall depletion on a yearly basis. This has motivated studies to determine methods and processes which can reduce the amount of ozone depletion.

This study examines the use of alternate propellants to reduce the production of PORCs. The methodology is straightforward. The composition of a current solid rocket is examined and those chemical species which are classified as PORCs are identified. Alternate propellants are identified which reduce or eliminate the production of those PORCs. Not surprisingly, some of the exhaust species produced by the alternate propellants are classified as PORCs. The amounts of the species are quantified and found to be acceptably small. The technology status of these propellants and the rocket engines that would utilize them is briefly summarized. The safety, handling and toxicity characteristics of alternate propellants are presented.

2.0 Utilization of Alternate Propellants to Reduce Production of PORCs

2.1 Identification of Chemical Species Relevant to Ozone Depletion and Other Environmental Issues

Typical solid propellant rockets produce primarily H_2O , CO_2 , Al_2O_3 , HCl and other species in lesser amounts. Of these species HCl has been identified as a PORC. By itself, HCl is not a concern in ozone depletion chemistry (Ref. 2-1). HCl is tightly bound and the photolytic cross section is relatively small. This results in an atmospheric residence time of a few days. Detailed stratospheric chemistry calculations including HCl suggest that it does not contribute substantially to ozone depletion. Unfortunately, the chemistry of the high temperature, afterburning shear layer at the plume intrinsic core/atmospheric interface converts some of the HCl to Cl_2 which is highly photoreactive. Cl_2 participates the Rowland-Molina reaction chain and depletes ozone locally. And, as is now known, the Cl atoms are reused many times, destroying many ozone molecules in the process. Oxides of nitrogen, NO_x , have also been identified as PORCs. NO_x has been identified as an important species in photochemical smog production for years and if produced in sufficient quantity by a rocket engine may be a concern in ozone depletion as well.

Likewise H_2O is a species of concern as a PORC. Water can condense at stratospheric altitudes, and in the condensed phase can participate in heterogeneous ozone depletion reactions, Ref. 2-1. It is certainly true that the amount of water produced by rockets is small compared to that produced by conventional power generation but if alternate propellants can be identified which reduce the amount of H_2O produced such information may be useful. Conventional solid propellant rockets also produce Al_2O_3 in solid or liquid phase. If heterogeneous ozone depletion chemistry is a concern, then the smaller Al_2O_3 particles in the size distribution as well as condensed liquid Al_2O_3 could both participate in local heterogeneous ozone depletion chemistry. Similar objections may be raised against propellant combinations which produce particulates as part of the exhaust stream or as a consequence of afterburning, such as carbon or soot. Carbon dioxide, CO_2 and carbon monoxide, CO , are not concerns as PORCs. However, there is a continuing discussion within the scientific community about the role of greenhouse gases as part of the global warming environmental issue.

Utilization of alternate propellants can reduce or eliminate each of these chemical species, individually or in combination, depending on the specific propellant combination selected. Since all propellants are part of a propulsion system, there is a cost implication whenever any part of the system is modified. However, it is possible to identify a range of alternate propellant combinations with differing impacts on propulsion system hardware. Some of the propellants identified will require relatively minor modifications to existing propulsion systems, other propellant combinations are technologically mature but require existing engine technology which is not currently in production in this country for boost-to-LEO applications. Finally there are propellant combinations which have been laboratory or test stand fired but have never been used in operational systems.

The fact that there are several potential propellant combinations available which may be useful for launch systems responsive to reduced PORC production is desirable. It enables the time phased implementation of different technology solutions with different launch system hardware and cost impacts. This provides flexibility in implementing solutions to the problem of stratospheric ozone depletion. For example, if existing solid propellants can be reformulated to include afterburning suppressant chemicals which reduce or eliminate HCl to Cl_2 conversion, this may be an

environmentally acceptable solution. If, at some future time, it is necessary to remove HCl entirely, either nitrate/carbonate based solid propellants may be introduced or conventional liquids, LOX/LH₂ and LOX/RP-1 maybe used in place of solid propellants based on ammonium perchlorate aluminum. If the Isp of the non-perchlorate solids is deemed too low for boost applications (which appears likely), or the concerns about heterogeneous ozone depletion due to H₂O mandate its elimination as a plume constituent, advanced fluorine based solid or gelled propellants can be brought on line, given sufficient development resources and schedule. There are a variety of potential mitigations to the problem of ozone depletion due to PORCs.

2.2 Identification of Alternate Propellants Which Reduce or Eliminate Formation of Selected PORCs

Detailed reactive flow calculations on the depletion of stratospheric ozone have identified chemical species that are classified as PORCs (Ref. 2-1). Several of these species can be identified as constituents in rocket plume exhausts, either in the primary exhaust stream, such as HCl, or as reaction products of the plume/atmospheric chemistry, such as NO_x and Cl₂. One strategy to reduce the amount of PORCs produced is to change the exhaust stream composition by using alternate propellants. Propellant combinations can be identified which do not produce selected chemical species or modify the plume chemistry so that certain classes of chemical reactions, such as afterburning, do not take place. Table 2.2-1 summarizes the ozone depletion effect to be mitigated, such as Cl₂ production, the method of mitigation, such as suppression of HCl reaction in the plume/atmosphere shear layer, the hardware implementation, i.e. change the solid propellant formulation by inclusion of alkali salts, and an indication of the hardware technology status of the implementation, i.e. studies, lab or bench scale experiments, test stand or operational system. Each of the rows of the table are discussed in subsequent sections. All discussions relating to the last column in the table, "Hardware Technology Status", are grouped together in section 2.2.5

Table 2.2-1 Summary of Ozone Depletion Mitigation Approaches Utilizing Advanced Propellants

Ozone Depletion Effect Mitigated	Method of Mitigation	Hardware Implementation	Hardware Technology Status
Reduce/Eliminate C_{12} Production	Suppress HCl Reaction in Shear Layer	Modify Existing Solid Propellant Formulations to Include Afterburning Suppressants	<p>Modifying Solid Propellant Formulations-Operational</p> <p>Identification of Afterburning Suppressants-Study and Lab/Bench Scale</p>
Remove HCl from Plume Exhaust	<p>Utilize Other Propellants- Solid Propellants Without Chlorine, i.e. Replace AP with Nitrate or Carbonate Based Oxidizers</p> <p>Conventional Liquids LOX/LH₂, LOX/RP-1</p> <p>Advanced Liquids based on Fluorine Oxidizers- LF₂/LH₂ or LF₂/N₂H₄ or Others</p> <p>Advanced Solids Based on Fluorine Oxidizers - NF₄BF₄/ PNF₂/B or Other Fuel</p> <p>Advanced Gels Based on Conventional Oxidizers- i.e. HNO₃ + LiNO₃ + SiO₂ (gel)/ MMH + Al (gel)</p> <p>Advanced Gels Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄+B (gel)</p> <p>Advanced Hybrids Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄ (liquid)</p>	The Utilization of Alternate Propellants Requires Development of a New Engine System	<p>Solid propellant oxidizers containing no chlorine have been test stand fired, although not at the thrust levels required for boost to LEO applications. There is a significant reduction in the Isp.</p> <p>LOX/LH₂ and LOX/RP-1 liquid rocket engine technology is flight demonstrated. It is currently not in production in this country for boost to LEO systems. It is in production in other countries in the world.</p> <p>Advanced liquid propellants based on fluorine, F₂, ClF₃, ClF₅, FLOX and others, have been test stand fired in both the US and CIS. Turbo-pumped, upper stage engines have been developed and test stand fired in the CIS</p> <p>Advanced solid propellants based on fluorine oxidizers have been fired as heterogeneous F₂ gas generators in the US</p> <p>There have been considerable development of hybrids and gels, (although not with fluorine based oxidizers) in the US. Hybrids are flight demonstrated, gel propellants have been test stand fired, throttled and pulsed and may have achieved operational status for specific missions. None of these applications are at thrust levels necessary for boost to LEO missions. Gels and hybrids based on fluorine have not been developed</p>

Table 2.2-1 (Cont.)
Summary of Ozone Depletion Mitigation Approaches Utilizing Advanced Propellants

Ozone Depletion Effect Mitigated	Method of Mitigation	Hardware Implementation	Hardware Technology Status
Removal of Al_2O_3 to prevent ozone depletion due to heterogeneous chemical reactions	<p>Utilize Other Propellants-</p> <p>Conventional Liquids LOX/LH₂, LOX/RP-1</p> <p>Advanced Liquids based on Fluorine Oxidizers- LF₂/LH₂ or LF₂/N₂H₄</p> <p>Advanced Solids Based on Fluorine Oxidizers - NF₄BF₄/ PNF₂/B</p> <p>Advanced Gels Based on Conventional Oxidizers- i.e. HNO₃ + LiNO₃ + SiO₂ (gel)/ MMH+Al (gel)</p> <p>Advanced Gels Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄+B (gel)</p> <p>Advanced Hybrids Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄ (liquid) or Other Fuel</p>	The Utilization of Alternate Propellants Requires Development of a New Engine System	<p>LOX/LH₂ and LOX/RP-1 liquid rocket engine technology is flight demonstrated. It is currently not in production in this country for boost to LEO systems. It is in production in other countries in the world.</p> <p>Advanced liquid propellants based on fluorine, F₂, ClF₃, ClF₅, FLOX and others, have been test stand fired in both the US and CIS.</p> <p>Advanced solid propellants based on fluorine oxidizers have been fired as heterogeneous gas generators in the US</p> <p>There have been considerable development of hybrids and gels, (although not with fluorine based oxidizers) in the US. Hybrids are flight demonstrated, gel propellants have certainly been test stand fired and may have achieved operational status for specific missions, although not at boost phase to LEO thrust levels. Gels and hybrids based on fluorine have not been developed.</p>
Removal of H ₂ O to prevent ozone depletion due to heterogeneous chemical reactions	<p>Utilize Other Propellants.</p> <p>Advanced Liquids based on Fluorine Oxidizers- LF₂/LH₂ or LF₂/N₂H₄</p> <p>Advanced Solids Based on Fluorine Oxidizers - NF₄BF₄/ PNF₂/B or Other Fuel</p>	The Utilization of Alternate Propellants Requires Development of a New Engine System	<p>LOX/LH₂ and LOX/RP-1 liquid rocket engine technology is flight demonstrated. It is currently not in production in this country. It is in production in other countries in the world.</p> <p>Advanced liquid propellants based on fluorine, F₂, ClF₃, ClF₅, FLOX and others, have been test stand fired in both the US and CIS.</p> <p>Advanced solid propellants based on fluorine oxidizers have been fired as heterogeneous gas generators in the US</p>

Table 2.2-1 (Cont.)
Summary of Ozone Depletion Mitigation Approaches Utilizing Advanced Propellants

Ozone Depletion Effect Mitigated	Method of Mitigation	Hardware Implementation	Hardware Technology Status
Removal of CO ₂ to prevent contribution to greenhouse gas production and global warming	<p>Utilize Other Propellants. Advanced Liquids based on Fluorine Oxidizers- LF₂/LH₂ or LF₂/N₂H₄</p> <p>Advanced Solids Based on Fluorine Oxidizers - NF₄BF₄/ PNF₂/B or other fuel</p> <p>Advanced Gels Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄+B or other fuel (gel)</p> <p>Advanced Hybrids Based on Fluorine Oxidizers- i.e. F₂ (gel)/ N₂H₄ (liquid)</p>	The Utilization of Alternate Propellants Requires Development of a New Engine System	<p>LOX/LH₂ and LOX/RP-1 liquid rocket engine technology is flight demonstrated. It is currently not in production in this country. It is in production in other countries in the world. Advanced liquid propellants based on fluorine, F₂, ClF₃, ClF₅, FLOX and others, have been test stand fired in both the US and CIS.</p> <p>Advanced solid propellants based on fluorine oxidizers have been fired as heterogeneous gas generators in the US</p> <p>There have been considerable development of hybrids and gels, (although not with fluorine based oxidizers) in the US. Hybrids are flight demonstrated, gel propellants have been test stand fired and may have achieved operational status for specific missions, although not at boost phase to LEO thrust levels. Gels and hybrids based on fluorine have not been developed.</p>

2.2.1 Mitigation of Ozone Depletion by Reducing Cl Production

The first row in Table 2.2-1 considers existing solid propellant formulations. It has been mentioned that HCl is not by itself a concern but rather the afterburning of HCl to produce Cl₂ in the plume/atmospheric shear layer. This suggests that if afterburning in the shear layer could be suppressed then Cl₂ production would be reduced or perhaps eliminated. Afterburning suppression has been investigated by the plume physics community in relation to modifying the signatures of strategic missiles (Ref. 2-2). Several compounds have been which have been demonstrated to reduce/suppress afterburning in small lab scale combustors and rocket engines (Ref. 2-3). Alkali salts, such as KF, KCl, K₂SO₄, KNO₃, LiF, LiCl (and others), present in small quantifies (typically <1%, see Table 2.2-2) in the exhaust stream scavenge H atoms which initiate the afterburning chain reaction, thus quenching the afterburning reactions. This suggests that it may be possible to reformulate the solid propellant by relatively small additions of afterburning suppressant chemicals which would prevent conversion of HCl to Cl₂ in the shear layer.

By mixing the afterburning suppressant chemicals into the solid propellant, a uniform distribution of the suppressant is achieved. Previous attempts to incorporate alkali salts into liquid rocket engines have not provided uniform distribution of the afterburning suppressant chemicals and were not completely successful, Ref. 2-2. The technology status of solid propellants is operational and the modification of existing solid propellant formulations to obtain better performance is also operational. Potential afterburning suppressant chemicals have been identified in studies and lab/bench scale demonstrations (Ref. 2-4, 2-5, 2-6, and 2-7). There have been no demonstrations of

the efficiency of afterburning suppressant chemicals added to AP based solid propellants under flow conditions similar to stratospheric pressure, temperature and ambient air composition. Given that AP/Al solid propellants reformulated with added afterburning suppressing chemicals offer the smallest propulsion system impact, it is recommended in Section 5.2 that such a study be under taken.

Table 2.2-2. Typical Mole Fractions Necessary to Achieve Afterburning Initiation (Ref. 2-3)

Afterburning Suppressant Chemical	Mol % Required in Exhaust Products to Halve the Duration of Afterburning
KF	0.048
KCl	0.031
K ₂ SO ₄	0.036
KNO ₃	0.024
LiF	0.41
KBr	0.041

2.2.2 Mitigation of Ozone Depletion by Removal of HCl

The second row of Table 2.2-1 lists removal of HCl as the next most severe implementation of alternate propellants in mitigating ozone depletion. By removing HCl as a exhaust stream effluent, the effects of Cl on ozone depletion are eliminated. Implementing this step has more severe launch system hardware ramifications than reformulating the solid propellant to include afterburning suppressants. A new rocket engine will have to be developed or re-manufactured and the engine will have to be integrated into the launch system. There are several potential alternate propellants are identified: solid propellants that do not contain chlorine, conventional liquid propellants, LOX/LH₂ or LOX/RP-1, liquid propellants based on fluorine based oxidizers, solid propellants based on fluorine, gelled and hybrid propellants based on conventional acid oxidizers or fluorine. The hardware technology status of these approaches is discussed in Section 2.2.5.

The use of conventional liquid propellants is attractive in that concerns about HCl effects on ozone are eliminated. The engineering of rocket engines utilizing conventional liquid propellants is well understood and these engines have a history of operational success. These types of propellants produce CO₂, CO, H₂ and H₂O as combustion products. It is possible that thermal NO_x is formed as a consequence of afterburning in LOX/RP-1 systems. Calculations presented in Section 3.0 suggest this has a small effect on ozone depletion. There are continuing concerns and evolving understanding about the importance of H₂O condensation forming sites for heterogeneous ozone depletion chemistry in the plume. However, should it be case that HCl must be removed from the propellants, launch systems based on conventional liquid propellants are a credible alternative. Even if it is the case that conventional liquids are ultimately unsatisfactory due to heterogeneous ozone depletion due to H₂O, launch systems based on conventional liquids are the only demonstrated technology available in the near term (i.e. <5 years) which could conceivably replace conventional AP based solid propellants. While LOX/rubber hybrids are also potentially credible, they do not have the operational history that conventional liquid systems do. The same concern can be raised with existing gel propellants which are based on nitric acid oxidizers. All these carbon/ hydrogen/ nitrogen/ oxygen systems produce some amount of NO_x which has been identified as a

PORC. The NO_x can be produced either in the engine or in reactions in the atmospheric shear layer. Section 3 presents calculations of NO_x production for conventional liquid systems.

2.2.3 Mitigation of Ozone Depletion by Removal of Al₂O₃ and H₂O

The next two rows of Table 2.2-1 will be discussed together. These ozone depletion mitigation techniques are the next most severe and involve removing either or both H₂O and Al₂O₃ from the rocket exhaust effluent stream. The concern about H₂O is that upon condensation, water forms sites for heterogeneous ozone depleting reactions. The same concern can be raised about Al₂O₃. Since Al₂O₃ particles are generated as a distribution of sizes in the rocket engine combustion chamber, the smaller particles in the distribution can serve as sites for heterogeneous ozone depletion chemistry. Likewise, liquid Al₂O₃ can condense in rocket plumes and form sites for heterogeneous ozone depletion reactions.

Conventional liquid propellants are potential launch system implementations which eliminate Al₂O₃ only. If it is necessary to eliminate both Al₂O₃ and H₂O then advanced oxidizers will be required. Fluorine is prominent as a high performance oxidizer which forms combustion products such as HF which are not PORCs. HF is stable, with a strong H to F bond and has a low photolytic cross section. On the other hand, there are severe materials compatibility issues when using fluorine, and fluorine is highly toxic. It is not likely that liquid fluorine would be considered as a credible oxidizer in a launch system. There are solid propellants available using fluorine oxidizers which may be attractive. Oxidizers which are fluorine based, NF₄BF₄, have been identified and fired as F₂ heterogeneous gas generators, and fluorine based rubbers, PNF₂ have been known for decades. While much technology work has been done on the elements of a solid propellant motor using fluorine based oxidizers, considerable development is still required to field a boost-to-LEO fluorine based propulsion system.

2.2.4 Mitigation of Ozone Depletion by Removal of CO₂

At this time CO₂ is not identified as a PORC, but there is continuing discussion in the scientific community about the importance of greenhouse gases on global warming effects so mitigation of greenhouse gases by removal of CO₂ is considered. If it is concluded that CO₂ content in the plume should be minimized and that HCl must be removed and heterogeneous ozone depletion reactions are not a concern (so H₂O as an effluent species is acceptable), then conventional LOX/LH₂ propellants are adequate. It is possible that thermal NO_x can be created from LOX/LH₂ combustion in the afterburning shear layer. Calculations presented in Section 3.0 suggest this has a small effect on ozone depletion. As mentioned previously this technology is mature although currently not in production in the US at boost phase thrust levels.

If HCl, H₂O, and CO₂ all must be removed from the exhaust stream, the oxidizers based on fluorine must be considered. As mentioned above advanced launch systems based on liquid fluorine are unlikely for safety related reasons, but solid, gelled and even hybrid systems using fluorine oxidizers are acceptable for achieving ozone depletion.

2.2.5 Hardware Technology Status

Afterburning suppressants have been demonstrated in lab/bench scale tests studies as well as in studies (Ref. 2-2, 2-3, 2-8, and 2-9). Ref. 2-2 mentions demonstrations on small liquid engines using salt rods placed in the combustion chamber. Ref. 2-3 present data on a number of lab tests

tabulating the efficiency of compounds as to their ability to inhibit afterburning initiation. Ref. 2-8 has demonstrated afterburning shutdown by O/F variation which also eliminates formation of H atoms. Ref. 2-9 presents calculations on several advanced propellant concepts, such as $\text{LF}_2/\text{N}_2\text{H}_4$ and gelled ClF_5 with gelled N_2H_4 + metals, which do not afterburn if the O/F ratio is ~ 1 and the nozzle exit plane temperature is sufficiently low. All lab/bench and test stand demonstrations have been at much lower thrust levels than those required of boost to LEO systems.

Of all the approaches listed in the Table 2.2-1, reformulated conventional solid propellants with afterburning suppressants will have the least overall impact at the launch system level, supposing that suitable afterburning suppressants can be identified. Should a conventional solid propellant with suppressants be fielded successfully, and the new propellant is in place in a new booster engine, the change is transparent to the user infrastructure, if there is no substantial degradation of the Isp. Given that the mass fractions of afterburning suppressants would very likely be small, a few mass percent typically, the effect on Isp should be minimal.

Solid propellant oxidizers containing no chlorine have been contractor developed under USAF sponsorship and test stand fired (at AFRPL/AFAL, now the Phillips Lab, Edwards AFB). These firings were successful, although not at the thrust levels required for boost to LEO applications. There is a significant reduction in the Isp in replacing perchlorate oxidizers with nitrate/carbonate formulations. While it is credible that such formulations could be scaled to booster sized thrust levels, these boosters would be of different sizes than the solids of today because of the reduced Isp. In any event this would be a major engine development effort. The HCl would be removed from the plume exhaust. However, H_2O and Al_2O_3 would remain with any attendant environmental concerns related to those species.

LOX/ LH_2 and LOX/RP-1 liquid rocket engine technology is well developed and flight demonstrated, i.e. the F-1, SSME among many examples. This technology is currently not in production in this country for boost systems. All the heavy lift rocket engines currently used in the US are solid propellant based. LOX/ LH_2 and LOX/RP-1 engines (and launch systems) are available from other countries, particularly the CIS (Proton, Zenit, the SL-X series, etc.). However, there could be security issues surrounding the use of rocket engines provided to the US by a foreign country (not to mention a former cold war enemy) which may be used to launch classified payloads.

Though not currently in production, it is certainly true that liquid engine technology could be redeveloped and NASA has performed studies on the cost of re-manufacturing the F-1 or creating a new engine for boost to LEO applications. Other NASA programs, with the goal of developing low-cost-to-LEO launch systems, have test stand fired a 40,000 lbf LOX/ LH_2 , featuring: low cost turbo-pumps, relatively low Pc operation (~ 300 psia), single pintle injector, cast-in-place ablatively cooled chamber with $L^* \sim 50$ -100 in. Designs for other engines have been developed for thrusts up to 1,000,000 pounds, Ref. 2-10 and 2-11. These conventional liquid engines have acceptable specific impulse values. The LOX/ LH_2 engines have Isp ~ 425 + sec and LOX/RP-1 are ~ 280 +sec depending on design details.

Advanced liquid propellants based using fluorine based oxidizers, such as F_2 , ClF_3 , ClF_5 , FLOX, ClOF_3 and others, have been test stand fired in both the US and CIS. Even the RL-10 has been fired with FLOX/ CH_4 and F_2/H_2 (Ref. 2-12). Through the late 1960s and early 1970s test stand firings using these advanced oxidizers were not uncommon. The attraction of fluorine based

oxidizers has always high performance, with specific impulse values in the range of ~370 to 400+ sec depending on the engine configuration; ox/fuel selection, chamber pressure, O/F ratio and expansion ratio. This propellant technology fell out of favor in the US, given the stringent materials compatibility, safety and handling requirements associated with fluorine. The CIS (then USSR) continued development of 20,000 lbf turbo-pumped upper stage engines utilizing LF_2 and NH_3 fuel. "Energomash" was the engine developer. The engine Isp was ~400 sec. This design was ultimately test stand fired but never incorporated into operational systems. The use of fluorine as a flow medium for high power HF/DF chemical lasers provided the motivation to continue to develop materials compatibility and handling technology in the US. However, the handling procedures necessary for the safe utilization of liquid fluorine based oxidizers probably preclude them from use in boost to LEO systems. However, utilization of fluorine in some other form, such solid or gelled F_2 , may be attractive since both solid and gels are in wide use today and the safety and handling procedures are well understood. It is a fact that gels in particular, have such attractive handling characteristics they have been classified as insensitive propellants.

The combustion products in the plume exhaust of fluorine based oxidizers contain HF and H_2 for LF_2 oxidizer and N_2H_4 , NH_3 or LH_2 (or slush H_2) fuel. Given that a goal of moving to alternate propellants is to remove HCl from the exhaust stream ClF_3 and ClF_5 and other chlorine containing oxidizers would be not be acceptable. At this time HF is not identified as a PORC (Ref. 2-1) since it is stable molecule in the atmosphere and does not actively participate in ozone depletion chemistry. Its bond strength is high and photolytic cross section small. Since it may be desirable to reduce the amount of HF and/or F_2 injected into the atmosphere operation at low O/F ratio may be necessary. While this does decrease the Isp to around Isp~300 at O/F~1 the amount of HF is reduced by about 50%. Low O/F operation raises the question of afterburning the H_2 to H_2O and if this can be prevented.

Studies have been performed on afterburning shutdown based on the low O/F ratio combustion of fluorine based systems (Ref. 2-4, 2-8, and 2-9). In this work it was demonstrated that operation of fluorine systems at low O/F ratio both reduces the available H atoms as well as the gas stream temperature to the point where afterburning is shut down. Of course, should gelled or solid fluorine systems be utilized, afterburning suppressants could be added to the propellants.

Advanced solid propellants based on fluorine oxidizers have been fired as heterogeneous F_2 gas generators in the US. To be a credible solid propellant it is necessary to identify an oxidizer, fuel and binder. There are several oxidizers available, the most attractive being NF_4BF_4 . Fluorine based rubbers, such as PNF_2 are well known. Given that an oxidizer and binder are available a heterogeneous solid propellant utilizing a metal fuel is a natural development. These elements were incorporated into a solid propellant gas generator using NF_4BF_4 with Al fuel, which was used to generate F_2 , on the MADS (Modular Array Demonstration Program), a US Army laser development program. While it is true that no rocket engines of any substantial thrust have been developed using solid fluorine based oxidizers, there is sufficient previous technology development to suggest that it could be done. Thermochemical calculations based on estimated enthalpy of formation for NF_4BF_4 yield Isp estimates ~300 sec with an exhaust stream containing no particulates or condensed phase material.

There have been considerable development of hybrids and gels, (although not with fluorine based oxidizers) in the US. Hybrids are flight demonstrated. The HASP drones used liquid acid

oxidizer with fiberglass fuel, and AMROC in Camarillo, CA has developed LOX oxidizer/rubber fuel launch vehicles which have been test stand fired but, as yet, never launched. Gelled propellants also have a long development history. Gelled rocket engines have been test stand fired at the 15,000 lbf thrust range, throttled by factors of 10 in chamber pressure and pulsed to 4-6 msec. Gelled engine designs are part of US Army missiles currently under development (Ref. 2-13) and gel engines have been developed for USAF sponsored ejection seat programs. There has been much technology development and test stand firings but none of it at thrust levels sufficiently high for boost to LEO applications.

Gels based on fluorine based oxidizers have not been developed. The same observation can be made for hybrid systems but the case for liquid fuel with solid fluorine based oxidizers is stronger. The fluorine oxidizer, NF_4BF_4 and fluorine based rubber binder, PNF_2 are demonstrated. The elements of a potentially successful hybrid exist but have never been integrated into a propulsion system.

Rocket engine performance is always a consideration in the design of boost-to-LEO systems. Figure 2.1-1 shows the vacuum specific impulse as a function of O/F ratio for selected solid, conventional liquid, advanced liquid and gelled propellant combinations. These are equilibrium calculations with a chamber pressure of $p_c=100$ psia and area ratio $A/A^*=50$ nozzle. The conventional composite solid based on ammonium perchlorate/aluminum, AP/Al, provides a performance baseline comparison of ~ 320 sec under vacuum conditions. It is seen that liquids offer generally higher Isp values over a wide range of O/F ratios. This is desirable since it has been demonstrated in lab scale tests that rocket engine operation under fuel rich conditions reduces flame temperatures and H atom concentrations. These features enable afterburning shutdown under simulated stratospheric altitude conditions, (~ 25 km). Depending on the alternate propellant type considered, there may be either an Isp performance decrease or increase. The conventional liquid, LOX/RP-1 at O/F=1.6 with an Isp=320 sec shows a slight performance decrease relative to the solid propellant. Though not shown on the chart, solid propellants with nitrate or carbonate oxidizers have generally lower Isp's than the other propellants shown in the figure. Propellants utilizing cryogenic oxidizers such as LOX/LH2 or LF2/N2H4 at O/F ~ 1 have Isp's of $\sim 370+$ sec. LOX/LH2 engines are well known and have high Isp but low density implying large propellant volumes. Engines using fluorine based oxidizers have been demonstrated on test stands but not flown under operational conditions.

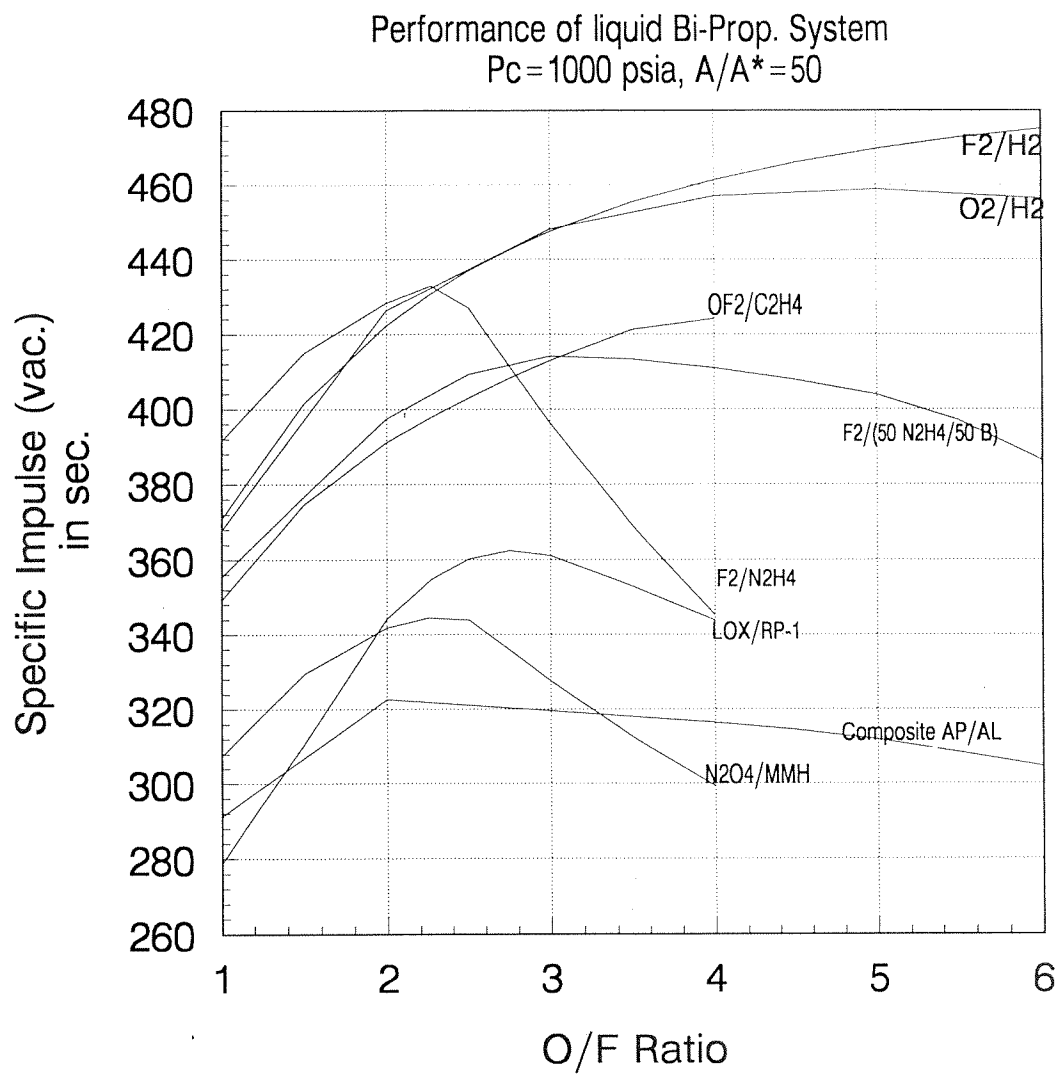


Figure 2.1-1

Performance of Liquid Bi-propellant Systems, $P_c = 1000$ psia.,
 $A/A^* = 50$

3.0 Calculations of Ozone Deletion from Conventional Solid and Alternate Propellants

3.1 Introduction

To assess the environmental impact from rocket launches calculations were performed for a conventional solid, two bipropellant liquids (LOX/LH₂ and LOX/RP-1) and a future advanced propellant system. Of particular interest is the environmental impact on stratospheric ozone due to the interaction of ambient air with rocket exhaust species. It is now known that exhaust species such as HCl, Clx, CO, H₂O, NOx, OH participate directly or indirectly in various catalytic cycles to destroy ozone in the gas phase. Particles such as H₂O and Al₂O₃ can also provide catalytic active sites for heterogeneous reaction to consume ozone. The essence of a catalytic cycle taking place as homogeneous gas phase reaction can be represented simplistically as



The reactive species X is regenerated in the second reaction (3-2), so that its participation of ozone removal is continuous and its abundance is unabated. Species such as Cl, NO, OH and H have been identified as the most important species for X.

3.2 Description of the Method of Analysis

Following the recent publication on the interaction of solid rocket exhaust with ambient ozone in the stratosphere (Ref. 3-1), the analysis of the plume is divided into two parts: the hot plume and the cold plume. In the hot plume calculation, the plume chemistry and gas dynamics are modeled starting from the combustion chamber in which chemical equilibrium is assumed, then followed by a one-dimensional streamtube reacting flow analysis for the flow in nozzle, and finally the finite rate chemistry analysis for the afterburning region downstream of the nozzle exit. The kinetic mechanism critical to the description of ozone-depletion species generation had been identified in Ref. 3-1, and is being adopted in these analyses. A variety of computer codes including the NASA Lewis developed Chemical Equilibrium Computer Program (CEC), Ref. 3-2, the JANNAF Solid Propellant Rocket Motor Performance Program (SPP), Ref. 3-3, and Standardized Plume Flowfield Code (SPF II), Ref. 3-4, were used to evaluate the production of these harmful species. In the cold plume regime, the chemistry is dominated by a set of kinetic reactions of ozone-depletion catalytic cycles (Eq. 3-1 and 3-2) and photodissociation reactions of byproducts from these catalytic cycles. The cold plume analysis is based on an axisymmetric plume with radial turbulent diffusion (Ref. 3-1). Tables 3-1 through 3-3 show the specifications for the conventional solid and bipropellant liquid rocket motor under consideration. These specifications include nominal 700,000 and 2.4 million lbf thrust classes of engines.

Table 3-1 Specifications of Solid Rocket Motor

Thrust (lb _f)	620,000	2.4 M
Chamber Pressure (psia)	1275	1000
Area Ratio	18.5	50
<u>Propellant Composition</u>		
Aluminum	19.0	
Ammonium Perchlorate	69.0	
R-45/IPDI	11.0	
DOA	1.0	

Table 3-2 Specifications of Liquid Rocket Motor

<u>Liquid H₂/LOX</u>		
Thrust (lb _f)	720,000	2.4 M
O/F Ratio	6.6	6.6
Chamber Pressure (psia)	300	1000
Area Ratio	7.0	50

Table 3-3 Specifications of Liquid Rocket Motor

<u>RP-1/LOX</u>		
Thrust (lb _f)	810,000	2.4 M
O/F Ratio	2.2	2.2
Chamber Pressure (psia)	300	1000
Area Ratio	7.0	50

3.3 Analysis Results and Discussion

The results of these analyses for the nominal 700,000 lbf class of engines are shown in Figures 3-1 through 3-3 for the solid, LH₂/LOx and RP-1/LOX systems respectively. Figure 3-1 shows the total mass flow rate from the solid rocket exhaust as a function of downstream location of the plume. The presence of an afterburning region where CO is converted into CO₂, H₂ to H₂O, and more importantly HCl to Cl₂, is clearly shown. The region extends about 3000 feet downstream at which no significant chemical reaction take place. From a local ozone depletion standpoint, the formation of Cl₂ from HCl in this region is significant because Cl₂ photodissociates into Cl readily in the presence of sunlight, which in turn can contribute to the depletion of local ozone through the Cl catalytic cycle (Eq. 3-1 and 3-2). The concentration of nitric oxide remains fixed to the level in the combustion chamber and no additional NO is formed in the afterburning region where temperature is relatively low. In addition, OH is completely consumed in reactions with H₂ or CO.

Figure 3-2 shows the centerline species concentration as a function of downstream locations for the LH₂/LOX system. Due to the fuel-rich condition, H₂ appears as a combustion product in the

exhaust and provides the necessary fuel to sustain burning in the afterburning region. The level of NO formed in the afterburning region is extremely low (1 ppb) and upon dilution due to air entrainment, the level drops to 10^{-3} ppb which is much lower than the ambient level in the stratosphere (10 ppb).

Figure 3-3 shows the centerline species concentration profiles for the RP-1/LOX system. Low production of NO in the afterburning region is also observed. In fact the level of NO is almost one order of magnitude lower than that of the LH₂/LOX system. Again due to fuel-rich condition CO appears as an exhaust product which is oxidized to form CO₂.

Table 3-4 summarizes the production of ozone depletion species for the rocket system under consideration.

Table 3-4 Comparison of Ozone-depletion Species Production(in Kg/s)

<u>Species</u>	<u>Solid</u>	<u>LH₂/LOX</u>	<u>RP-1/LOX</u>
HCl	200	0.0	0.0
Clx	750	0.0	0.0
NOx	7.0	10^{-6}	10^{-6}
HOx	1	10^{-3}	10^{-3}
H ₂ O	800	757	380

It is quite clear that solid rocket system is considerably more harmful to the stratospheric ozone than any of the two liquid bipropellant systems. Aside from the greenhouse gas consideration, the RP-1/LOX system is more benign than the LH₂/LOX system.

From a local impact standpoint, the effect on stratospheric ozone due to the bipropellant exhausts are equally unimportant, as shown in Figure 3-4 and 3-5. Figure 3-4 shows the cold plume centerline species concentration as a function of time. The analysis was performed assuming exhaust species deposition at an altitude of 30 km. The low ozone density hole appeared in the ozone concentration profile for early times is caused by a displacement effect rather than chemical consumption. Apparently, it takes about 50 seconds for diffusion to fill up the plume-displacement hole. Figure 3-5 clearly shows the absence of chemical reaction for ozone. The ordinate shows the difference between the total number of ozone molecules in the plume and the number of diffusing ozone molecules, which measured the destruction of ozone. For a length of 1 second, there was only one molecule of ozone consumed, indicating the absence of a local hole.

Also presented here is the results of the RP-1/LOX system shown in Figures 3-6 and 3-7. The system generates less nitric oxide species in the afterburning region and was seen to be qualitatively the same as the LH₂/LOX system. Both RP-1/LOX and LH₂/LOX systems produce approximately 10^{-3} ppb of ozone-depletion species such as NO and HOx. Figure 3-6 shows the centerline specie profiles indicating that at about 100 seconds the diffusion process is essentially completed. Due to the low concentration of nitric oxide, no significant ozone depletion can be detected in the plume. In fact, because of the presence of atomic oxygen in the plume, ozone is initially generated through a three body reaction; i.e.: $O + O_2 + M = O_3 + M$. Figure 3-7 shows the net rate of ozone loss in the plume at different times. Instead of depleting ozone, there was a production of the order of 10^{11} molecules/cc/sec up to 0.1 second.

Due to the predominance of Clx deposition, and to a lesser extent from the production of NO , the impact on local ozone reduction is significant for the solid propellant system. Figure 3-8 shows the species profiles as a function of time. The presence of a local ozone hole can easily be seen and it has lasted for as much as 2000 seconds. Judging from the liquid system calculations (Fig. 3-4) diffusion can only account for 50 seconds of the time. Therefore, a significant amount of ozone must have been consumed. Figure 3-9 clearly shows the presence of a hole which lasted for approximately 2000 seconds, and as much as 60% depletion taking place in a hole of radius about 1000 meters. Figure 3-10 shows the total ozone loss in a 1-cm length of plume. As much as 10^{21} molecules of ozone can be lost. Considering a 100 launches per year of any ammonium perchlorate based solid rockets, traveling through the stratosphere of approximately 25 km distance, this translates into an approximately 0.00001 % loss of the total ozone concentration. This global effect is not small considering mankind will certainly continue to have rocket launches, and the number of launches will also likely to increase.

Similar results were obtained for the 2.4 million lbf thrust rocket systems. The ozone depletion potential however should scale approximately by thrust since mass flow rate is proportional to thrust. Figures 3-11 through 3-20 show the results of the cold plume analyses for these propellant systems corresponding to LH_2/LOX , $\text{RP-1}/\text{LOX}$ and composite AP/Al . The results are seen to be qualitatively similar to those of the 700,000 lbf thrust engines. Little or no ozone depletion was observed for the LH_2/LOX and $\text{RP-1}/\text{LOX}$ systems. For the solid system however, the level of local ozone destruction is about a factor of 4 higher than that of the 700,000 lbf thrust engine. This factor is consistent with the thrust ratio of the two classes of systems.

3.4 Conclusions

According to these analyses, it is clear that solid propellant systems not only will create a local ozone hole from large deposition of Clx into the atmosphere but the long term global effect can be just as alarming. Current analysis have not included the potentially harmful effect due to large deposition of H_2O vapor or droplets into the basically dry stratosphere. The ozone depletion potential may be identified from two sources: namely, heterogeneous reaction on droplet surfaces in the form of polar stratospheric clouds commonly found in Antarctica; or homogenous reactions according to the OH catalytic cycle, particularly in the upper stratosphere where the abundance of $\text{O}_2(1\Delta)$ can convert H_2O into OH radicals.

The liquid bipropellant system considered in this analysis exhibit no deleterious effect on the environment. But they both suffer from the same problem as that of the solid system in the case of H_2O production. In addition, $\text{RP-1}/\text{LOX}$ system tends to burn on the rich side. There is also the potential formation of carbon soot in the exhaust, thus providing active sites for heterogeneous ozone conversion.

An alternate propellant system containing fluorine as the oxidizer may be of interest, at least from ozone-depletion standpoint. The exhaust species of this alternate propellant will consist of H_2 , HF , F_2 . The system appears to be benign from an ozone depletion perspective. A study of the kinetic rate data for HF conversion into F_2 reveals a much slower reaction than that of HCl in the case of solid rocket. Therefore HF is not likely to be converted to the same extent in the afterburning region. As for the F_2 , its rate of photodissociation is slow compared to that of Cl_2 . Therefore fluorine based systems as a whole, appear to be more benign than the two liquid systems.

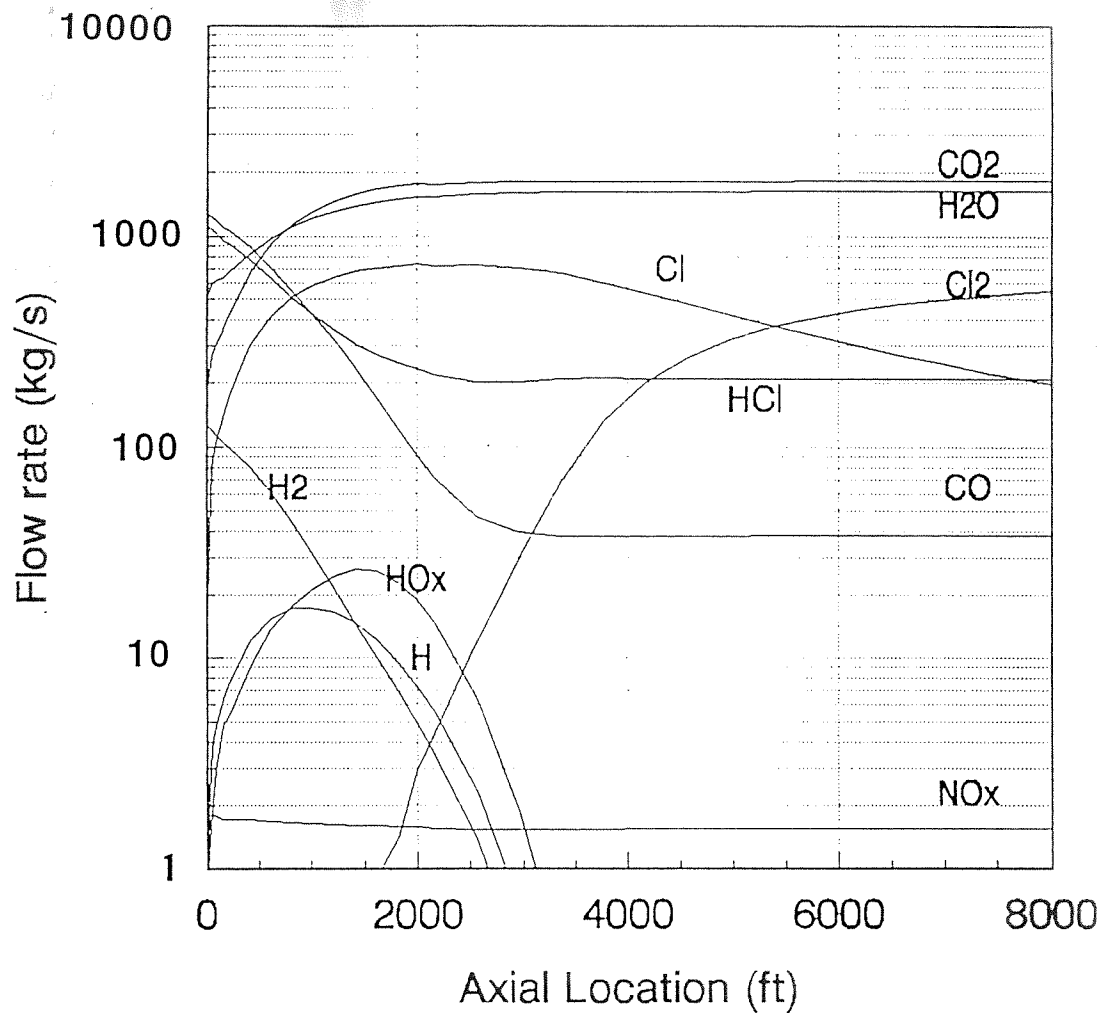


Figure 3-1 Exhaust Product Species Mass Flow Rates vs. Axial Location for 620k lbf Solid Propellant Rocket, Altitude = 30 km

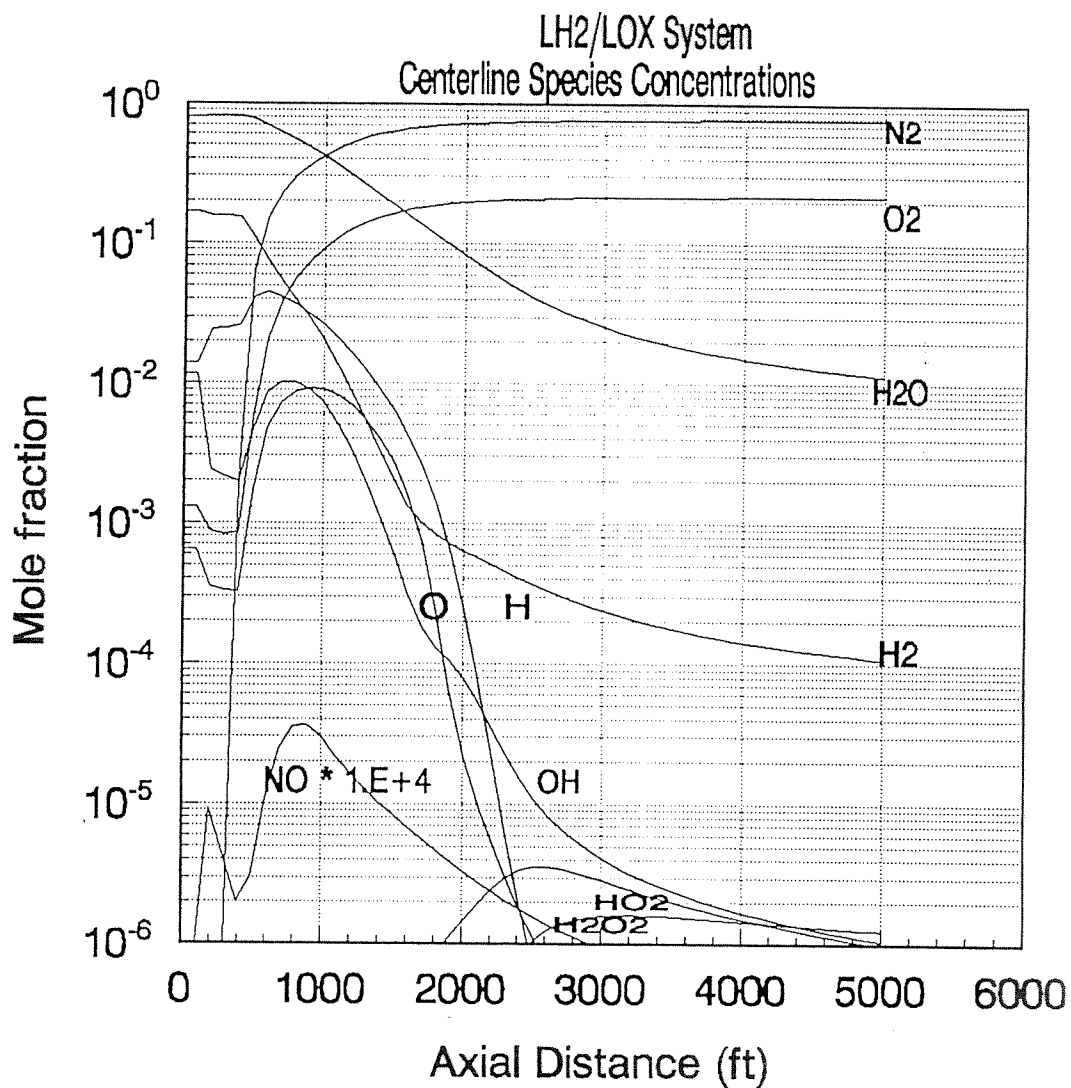


Figure 3-2 Exhaust Product Species Centerline Mole Fractions vs. Axial Distance for 720k lbf LOX/LH₂ Rocket

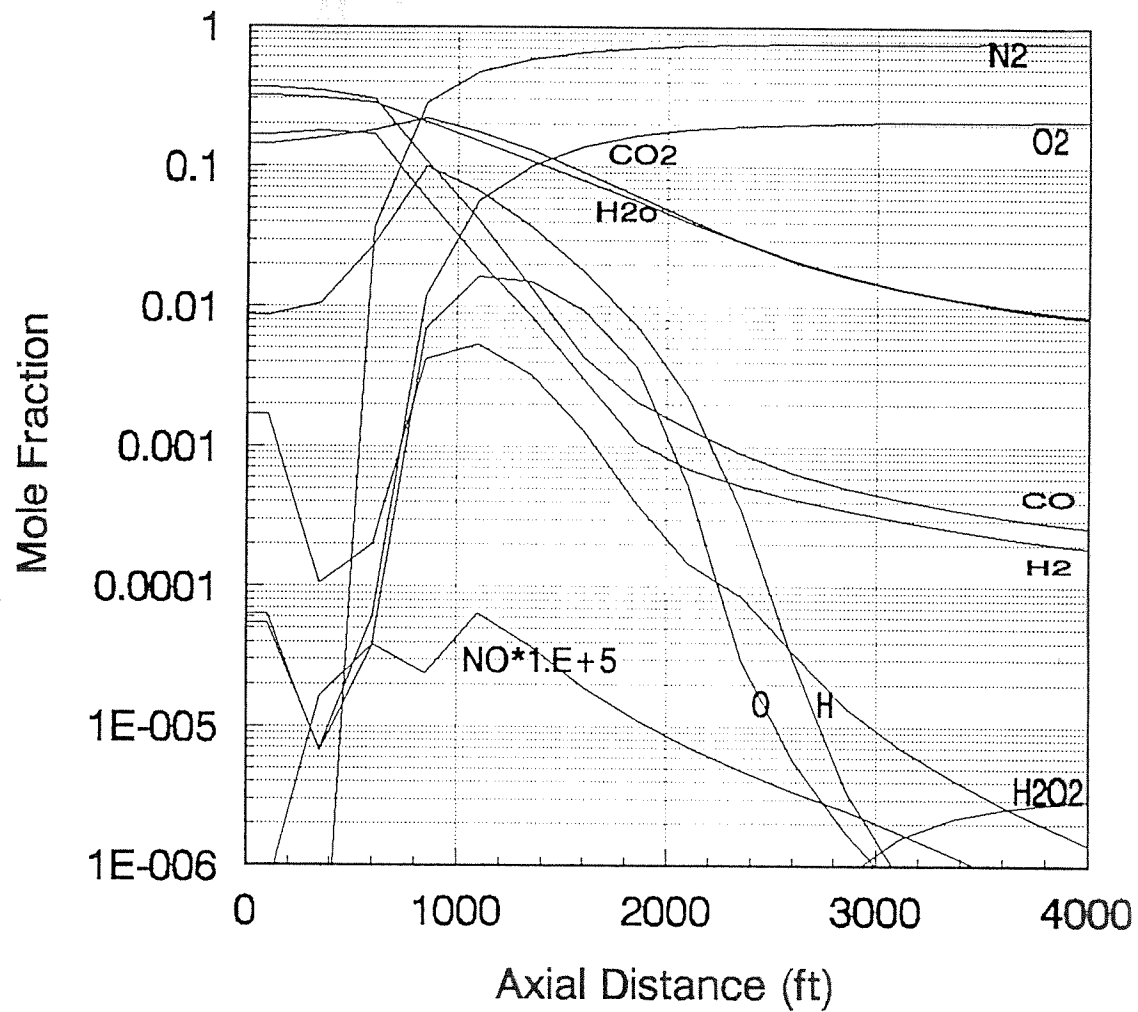


Figure 3-3 Exhaust Product Species Centerline Mole Fractions vs. Axial Distance for 810k lbf LOX/RP-1 Rocket

Centerline Density

LH2/LOX - 30 km

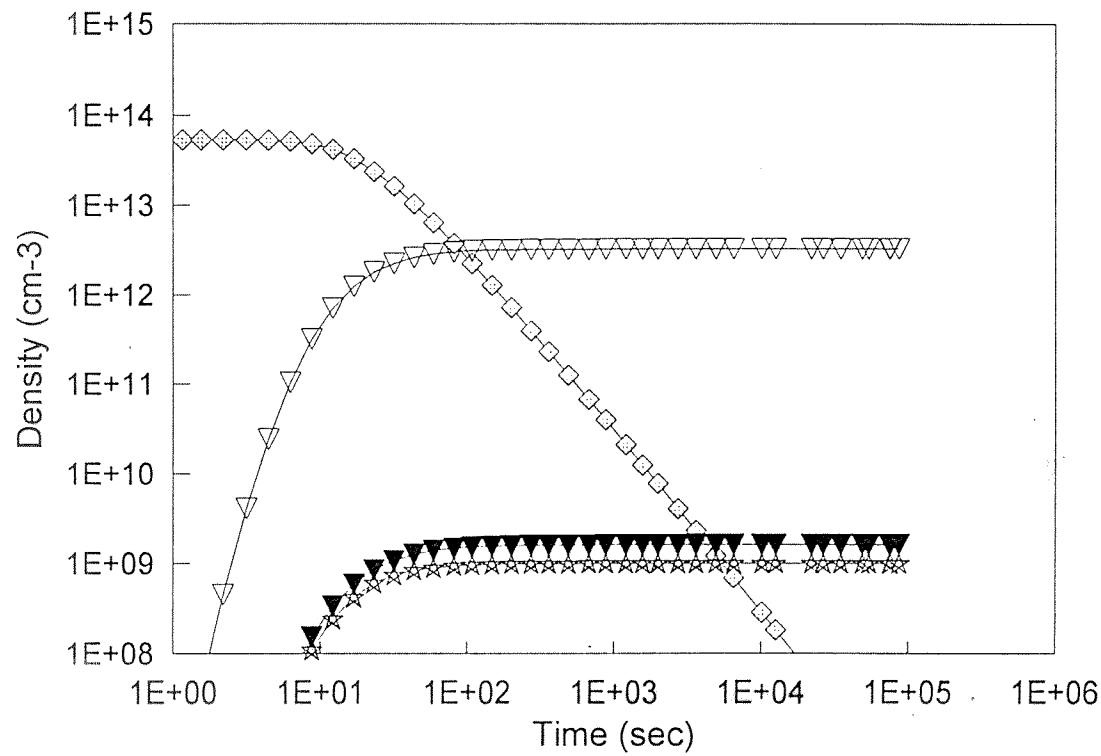


Figure 3-4 Centerline Densities vs. Time for 720k lbf LOX/LH₂ Rocket, Altitude = 30 km

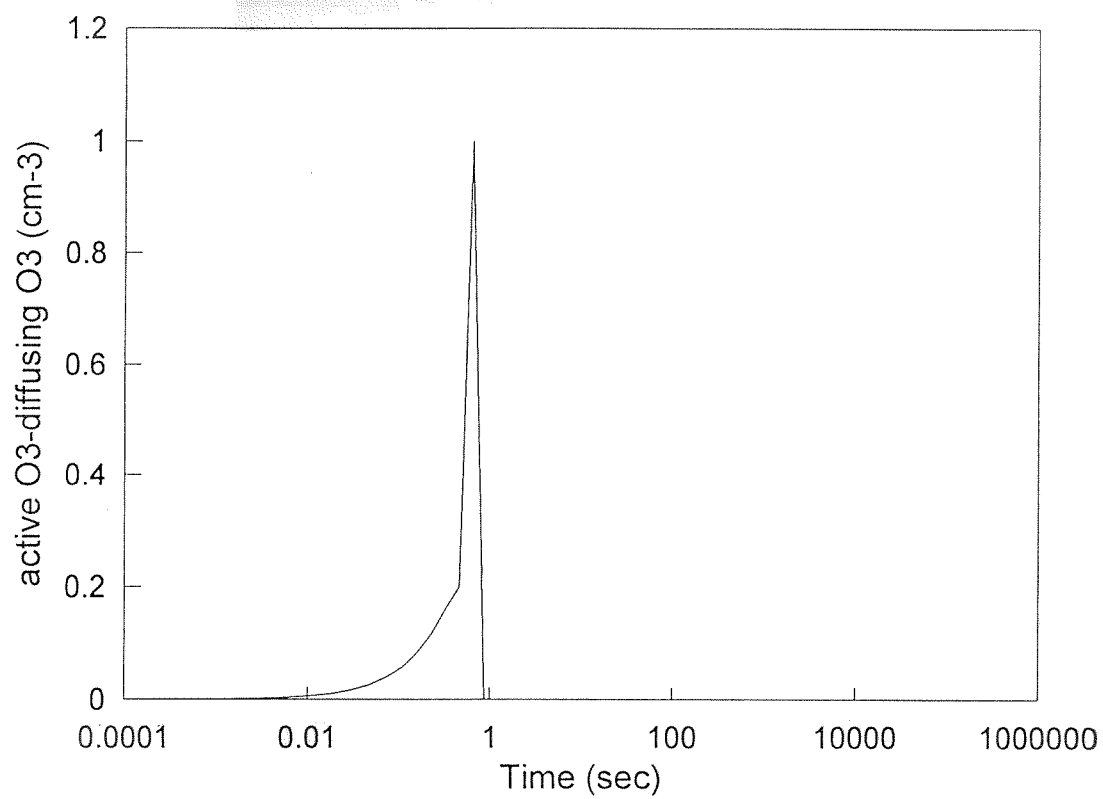
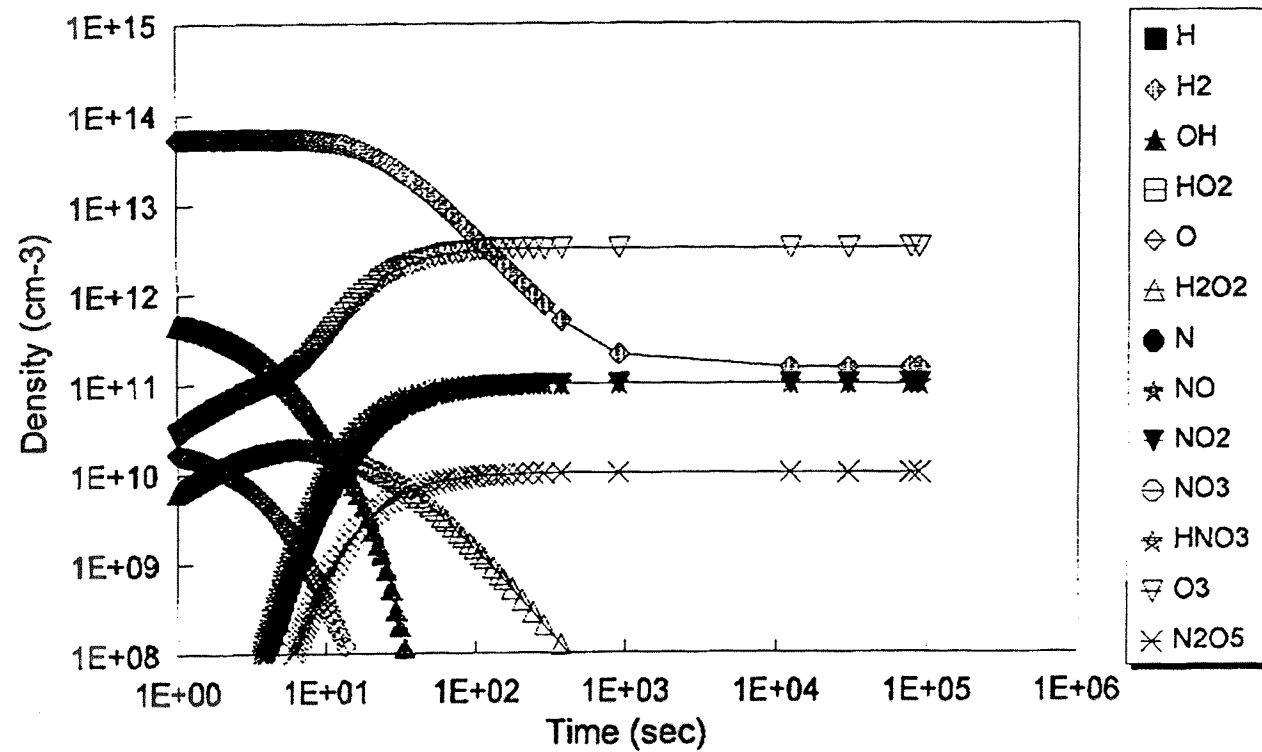


Figure 3-5 Net Ozone Depletion in 720k lbf LOX/LH₂ Rocket, Altitude = 30 km

Centerline Density

RP1/LOX - 30 km - 0.6 Mlb

Figure 3-6 Centerline Densities vs. Time for 0.6 M lbf RP-1/LOX Rocket, Altitude = 30 km



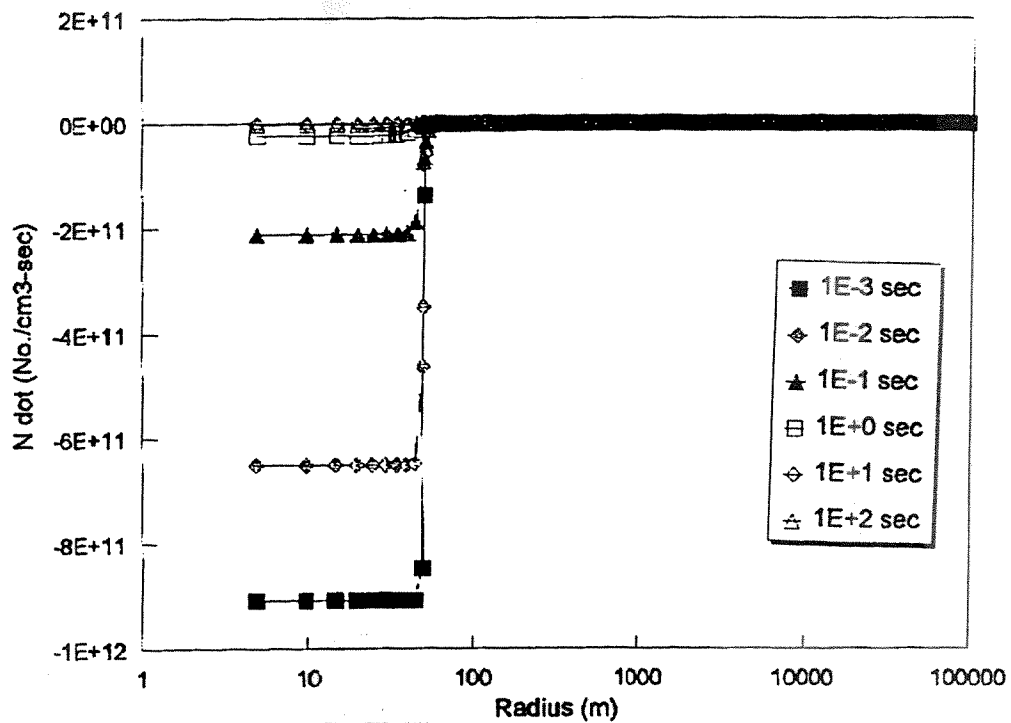


Figure 3-7 Net Ozone Depletion in 0.6 M lbf RP-1/LOX Rocket,
Altitude = 30 km

Centerline Density

Solid Rocket - 30 km - 180 m plume

Figure 3-8
Centerline Densities vs. Time for 620K lbf Solid
Propellant Rocket, Altitude = 30 km

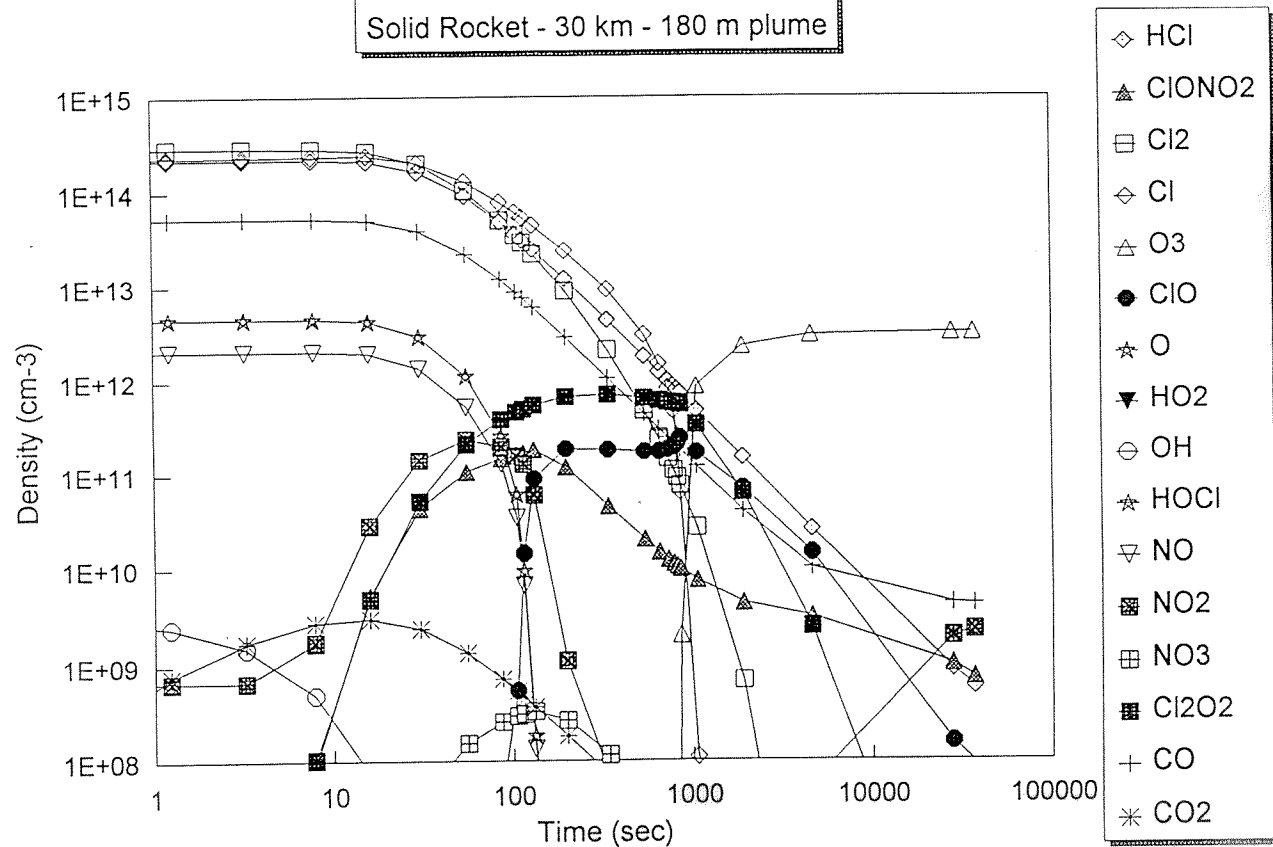
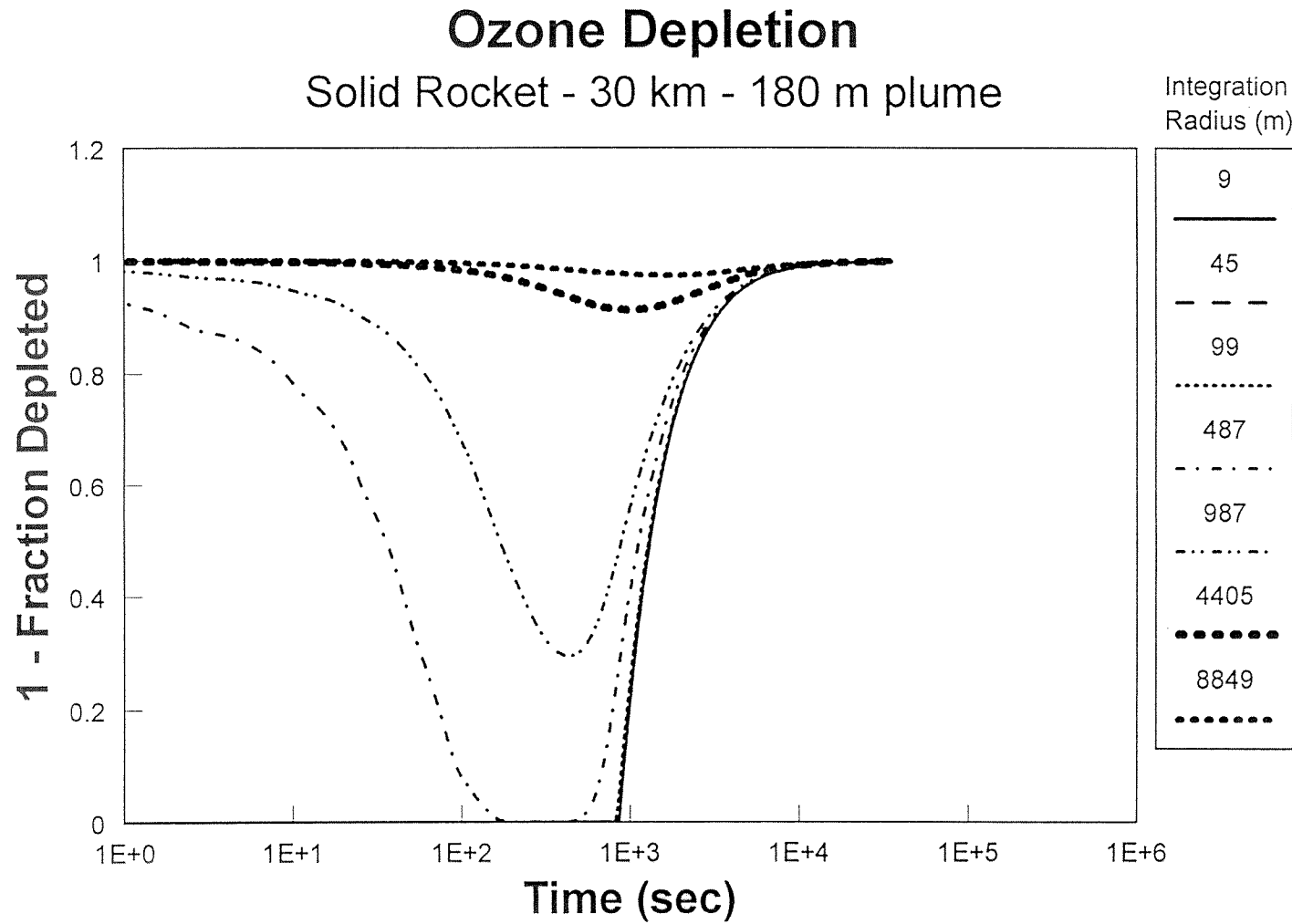


Figure 3-9 Ozone Depletion in 620K lbf Solid Propellant Rocket, Altitude = 30 km



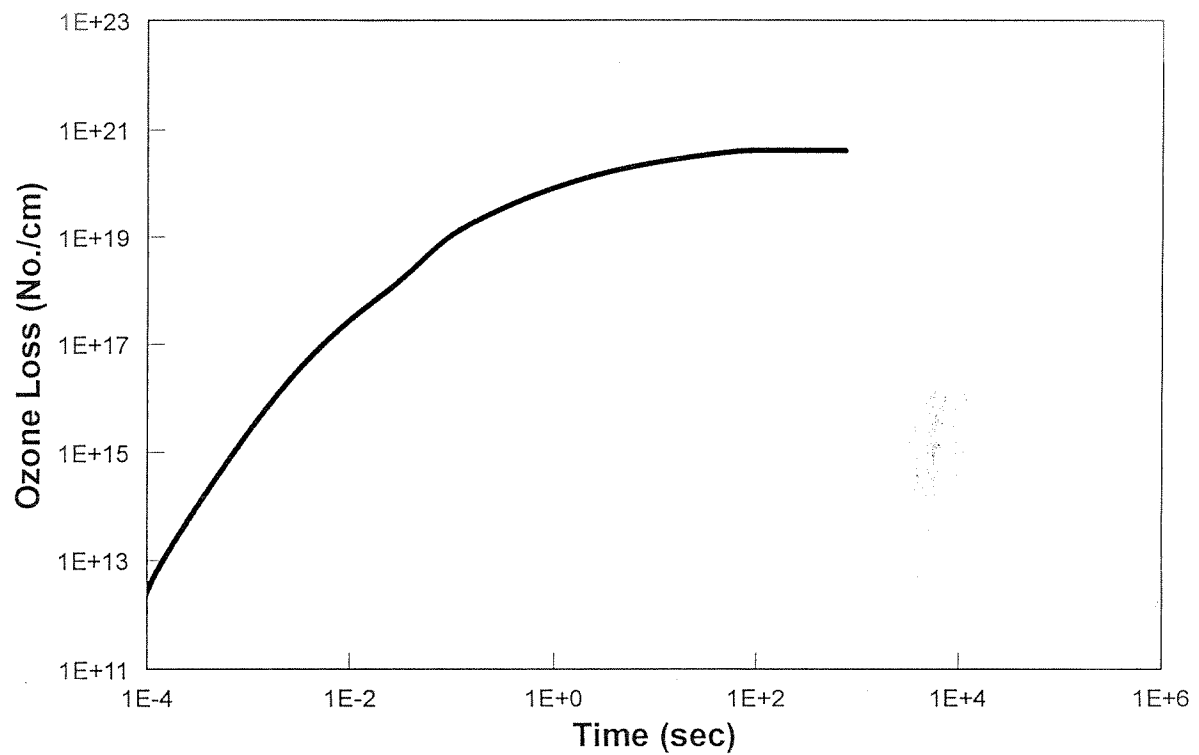


Figure 3-10 Net Ozone Depletion in 720k lbf LOX/LH₂ Rocket, Altitude = 30 km

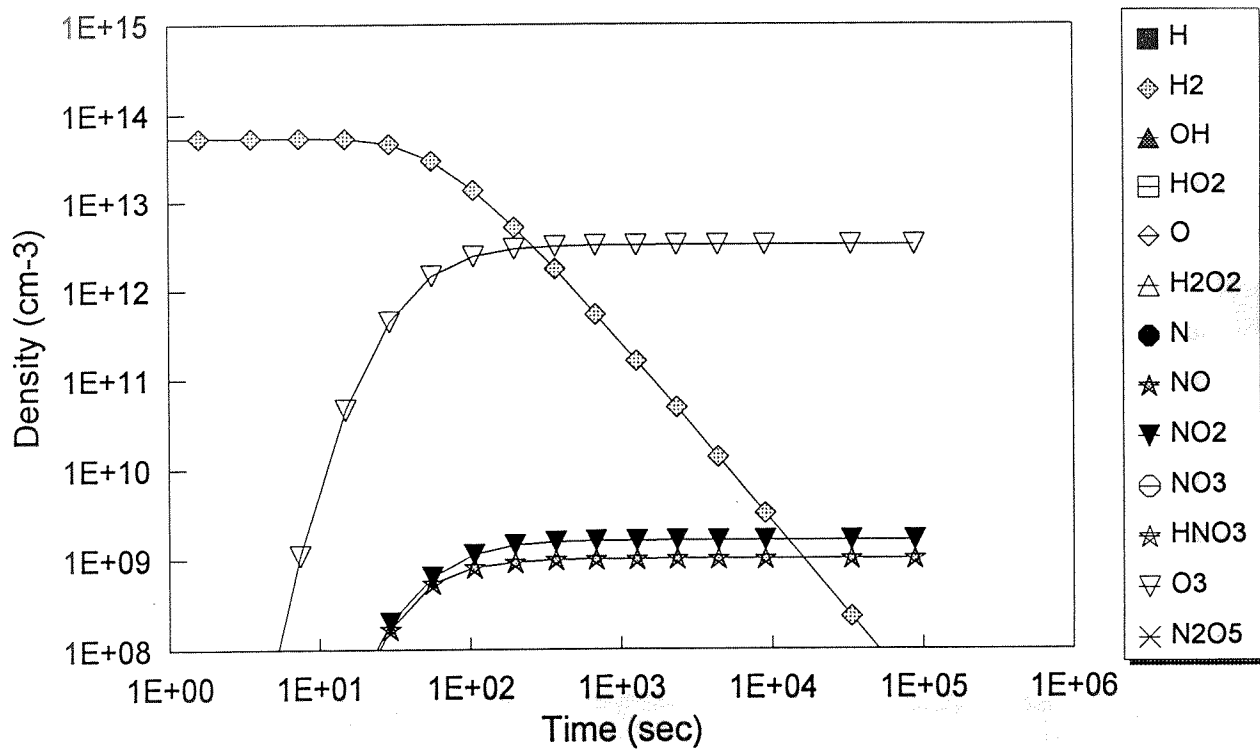


Figure 3-11 Centerline Density vs. Time for 2.4 M lbf LH₂/LOX Rocket, Altitude = 30 km

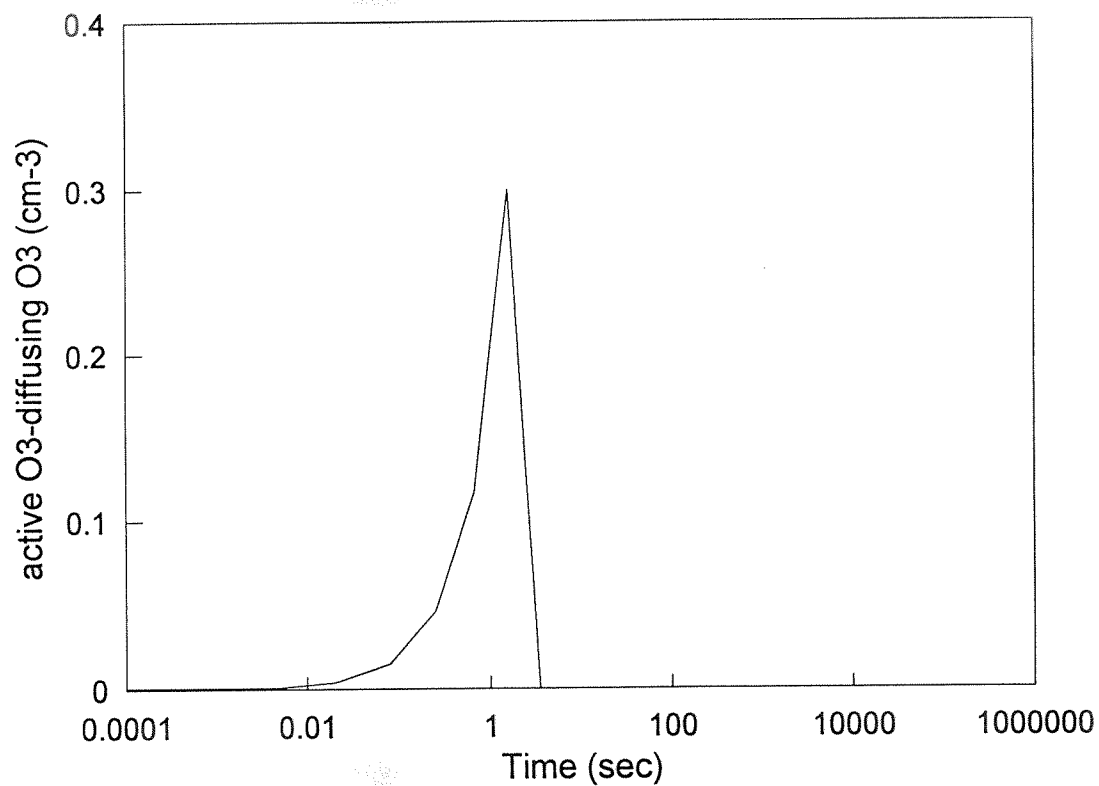


Figure 3-12 Net Ozone Depletion in 2.4 M lbf LH₂/LOX Rocket,
Altitude = 30 km

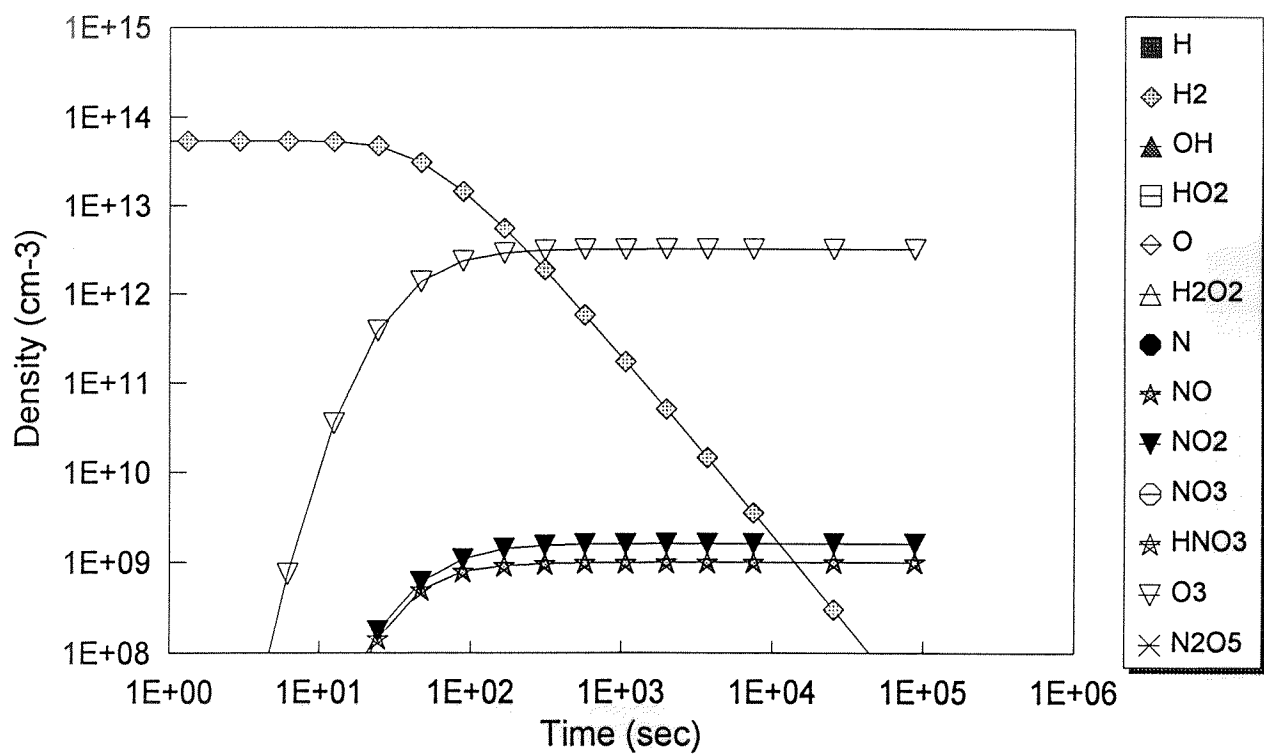


Figure 3-13 Centerline Density vs. Time for 2.4 M lbf RP-1/LOX Rocket, Altitude = 30 km

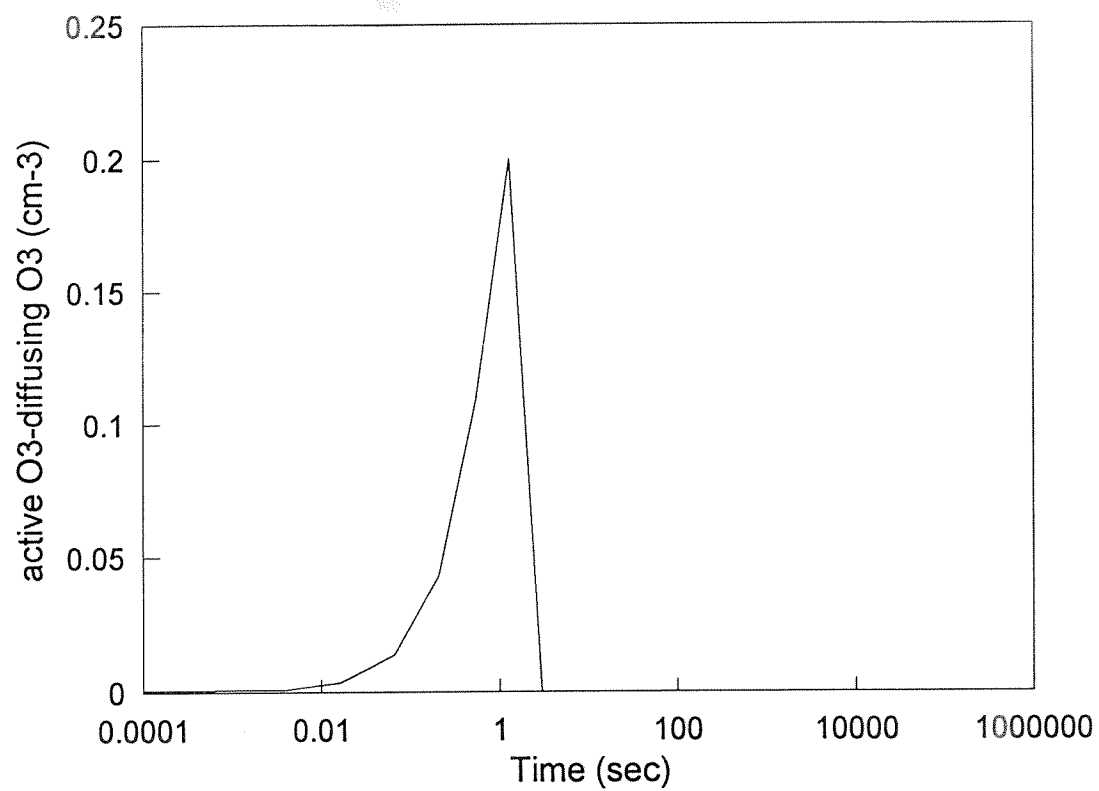


Figure 3-14 Net Ozone Depletion in 2.4 M lbf RP-1/LOX Rocket,
Altitude = 30 km

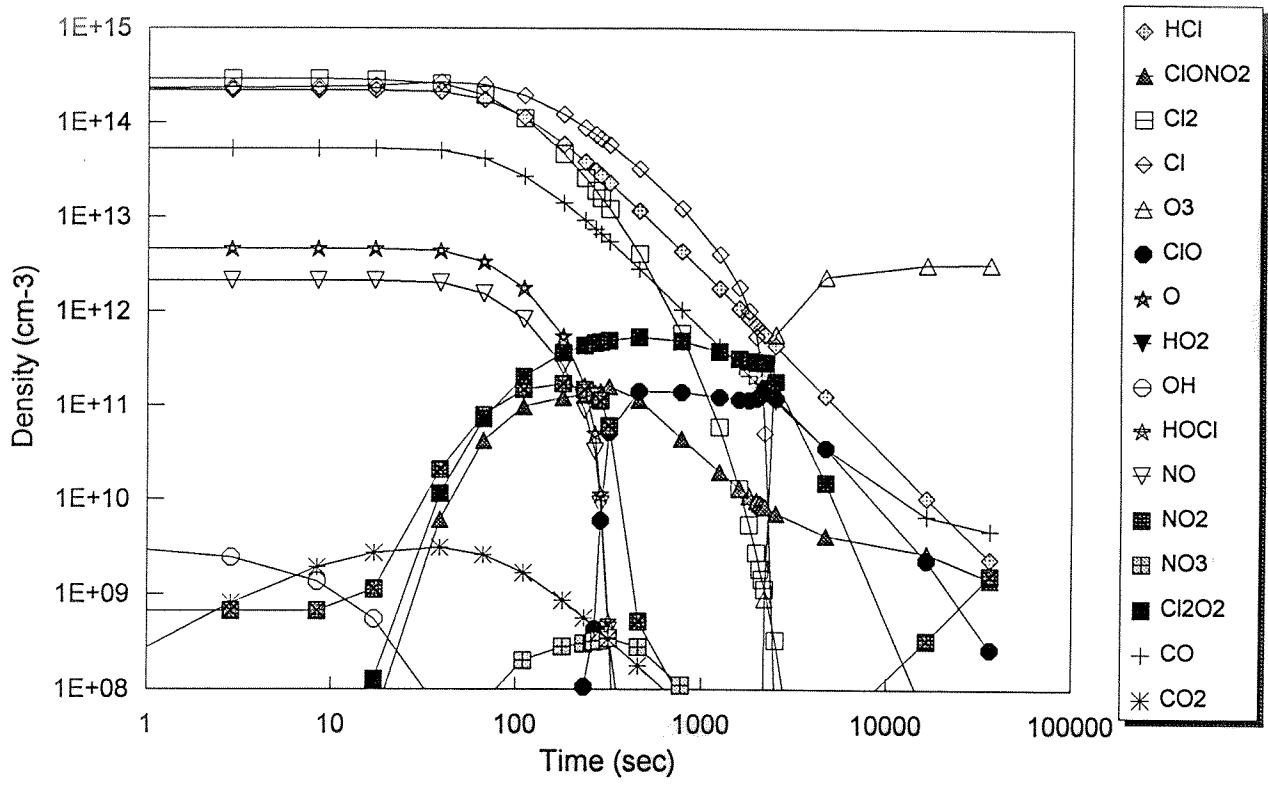
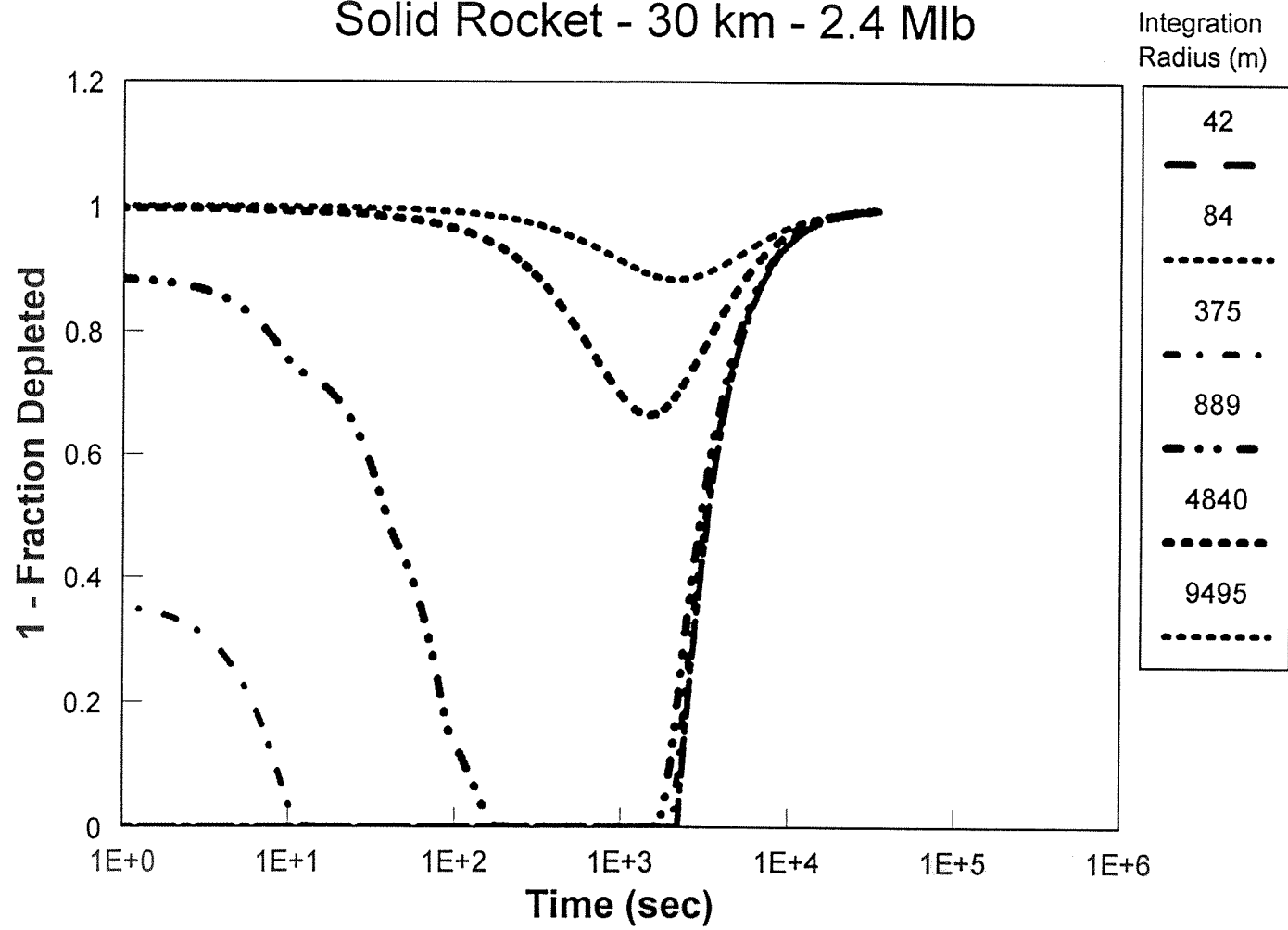


Figure 3-15 Centerline Density vs. Time for 2.4 M lbf Solid Rocket Motor, Altitude = 30 km

Ozone Depletion

Solid Rocket - 30 km - 2.4 MIb

Figure 3-16 Ozone Depletion for 2.4 M lbf Solid Rocket Motor,
Altitude = 30 km



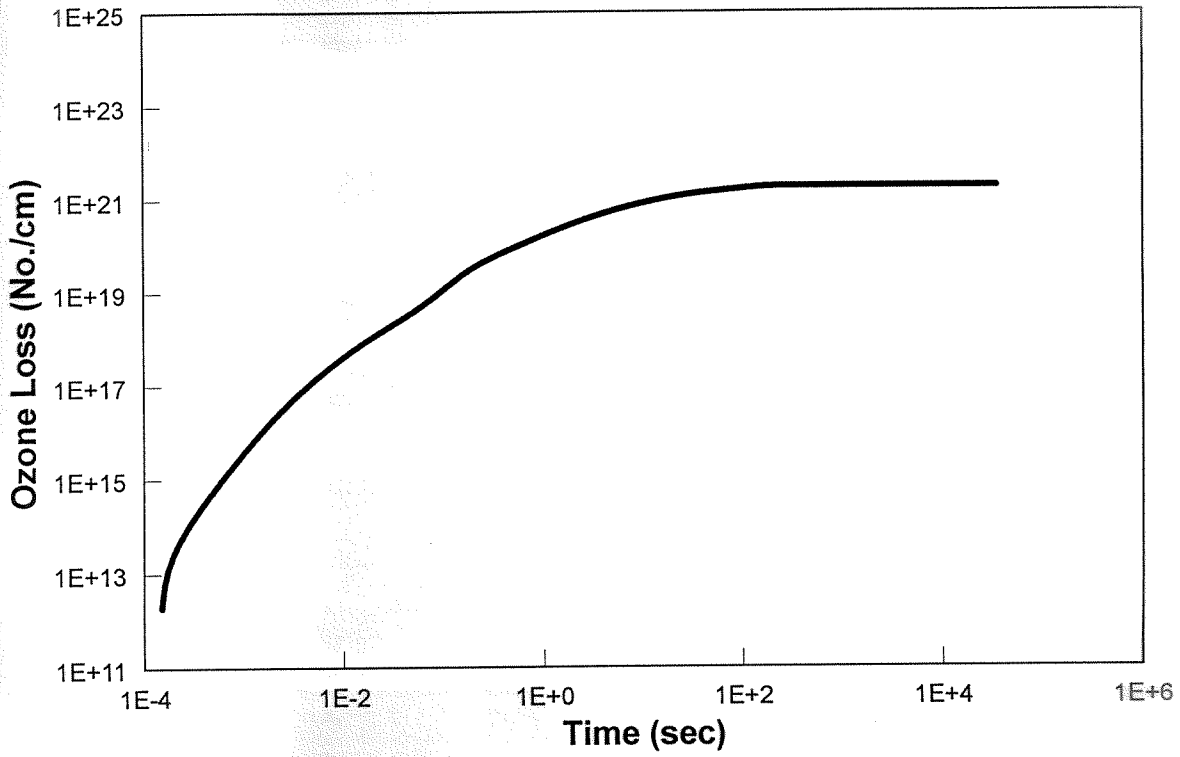


Figure 3-17 Net Ozone Depletion for 2.4 M lbf Solid Rocket Motor,
Altitude = 30 km

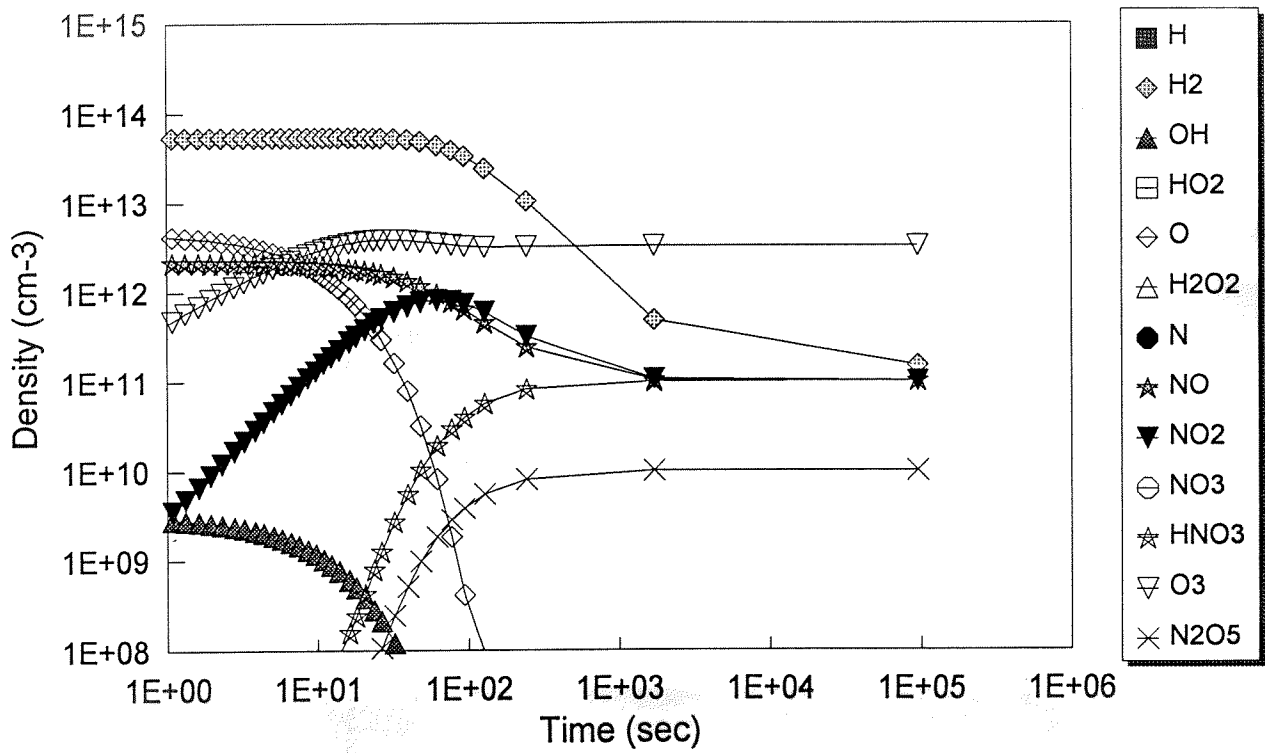


Figure 3-18 Centerline Density for 2.4 M lbf Solid Rocket Motor,
Altitude = 30 km

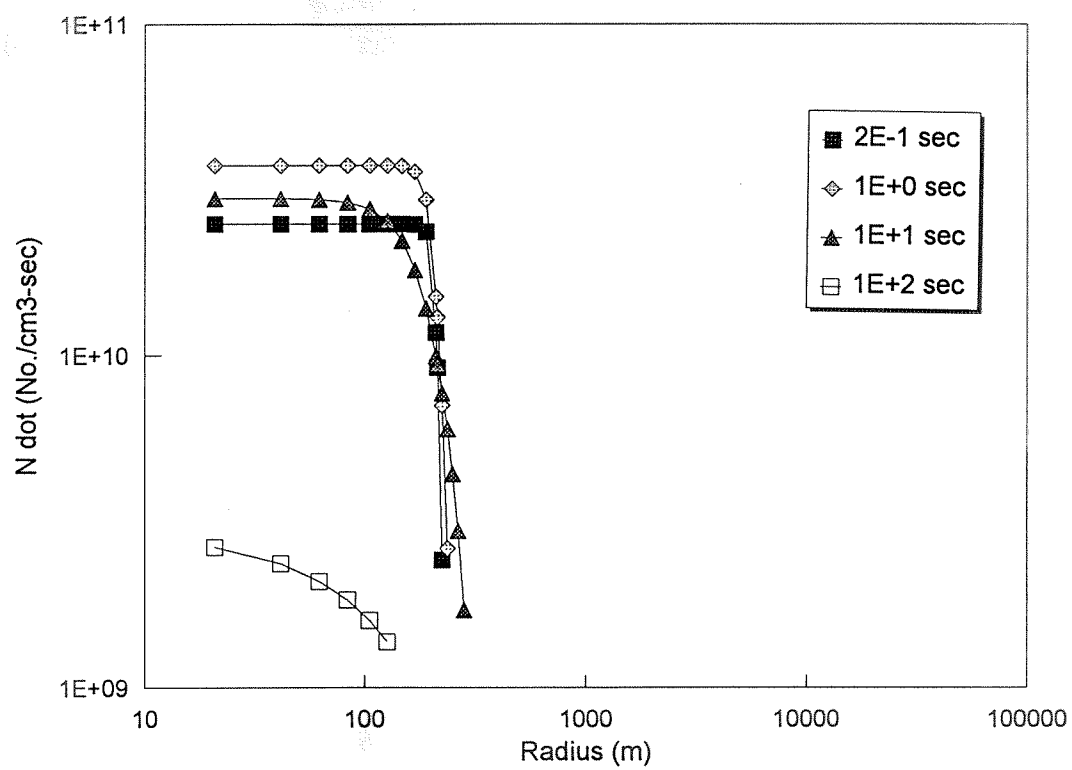


Figure 3-19 Radial Distribution of Net Rate of Ozone Depletion for
2.4 M lbf Solid Rocket Motor, Altitude = 30 km

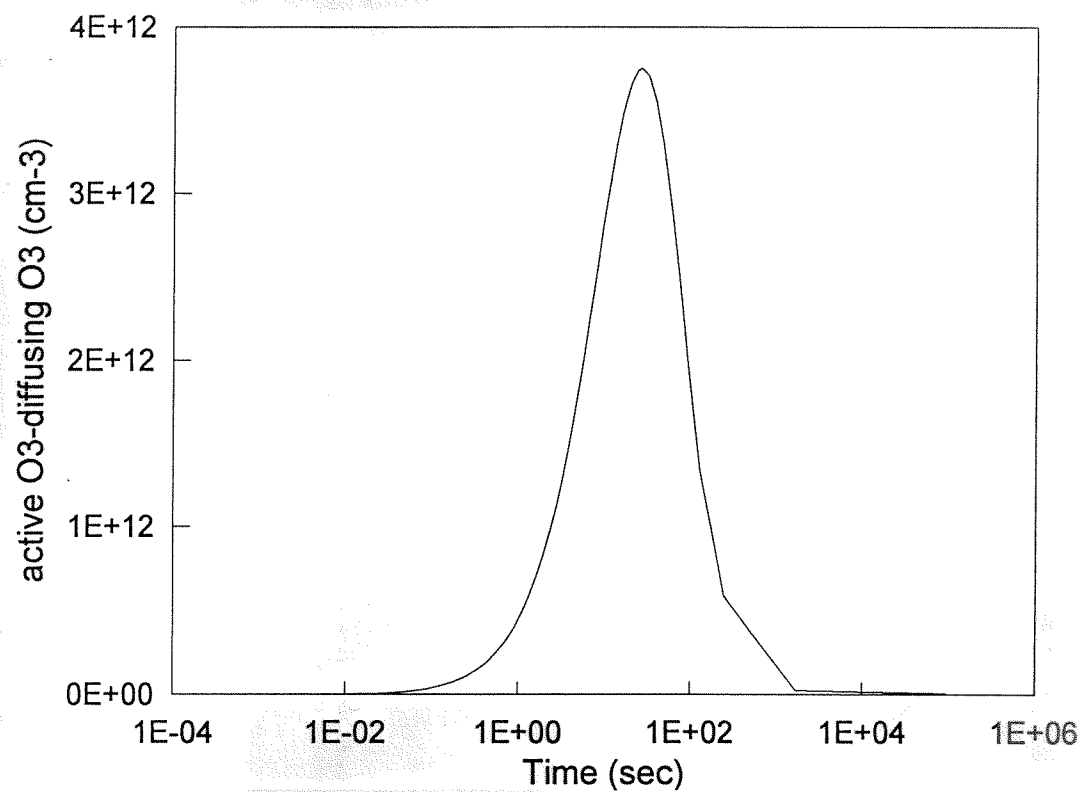


Figure 3-20 Net Ozone Depletion vs. Time for 2.4 M lbf Solid Rocket Motor, Altitude = 30 km

4.0 Propellant Assessment and Characterization

4.1 Introduction

This portion of the report is a compilation and analysis of safety, performance, and atmospheric environmental interactions due to combustion of rocket propellants during vehicle launches. This section includes propellant types/systems currently in use and those under development. It is prepared in compliance with Presidents Clinton's "The Climate Change Action Plan.", Ref. 4-1 "Federal Compliance with Right-To-Know Laws and Pollution Prevention Requirements.", Ref. 4-2, the "Emergency Planning and Community Right-To-Know Act.", Ref. 4-3; and the "Pollution Prevention Act ." of 1990, Ref. 4-4. There is a limited review of rocket propellant exhaust quantities from non-launched development testing. Safety and environmental effects of vehicle and propellant manufacture are not included. Also excluded are specific soil and water contamination considerations.

Overall, the goals of this project are to identify and describe the current and near future projected status of environmentally sensitive rocket propellants and launch systems — those that do not exhaust HCl or other gases that form acid rain and/or may cause or catalyze ozone depletion, do not exhaust or emit only small quantities of Al_2O_3 or other particulates, and exhaust only small quantities of "greenhouse gases." These criteria apply after the initial rocket exhaust plume undergoes afterburning between its constituents and the atmosphere, expands and cools to ambient pressure and temperature by mixing and by radiation and drifts with the wind. Practical criteria for these advanced propellants and systems are a minimum $I_{sp} > 280$ sec, safety for handling and storage relative to toxicity, corrosivity and explosion sensitivity, and minimum cost for implementation.

An outline of the structure logic of this report is presented in the flow chart, Figure 4.1-1. The section numbers of this report which discuss the specific topics are noted in the chart.

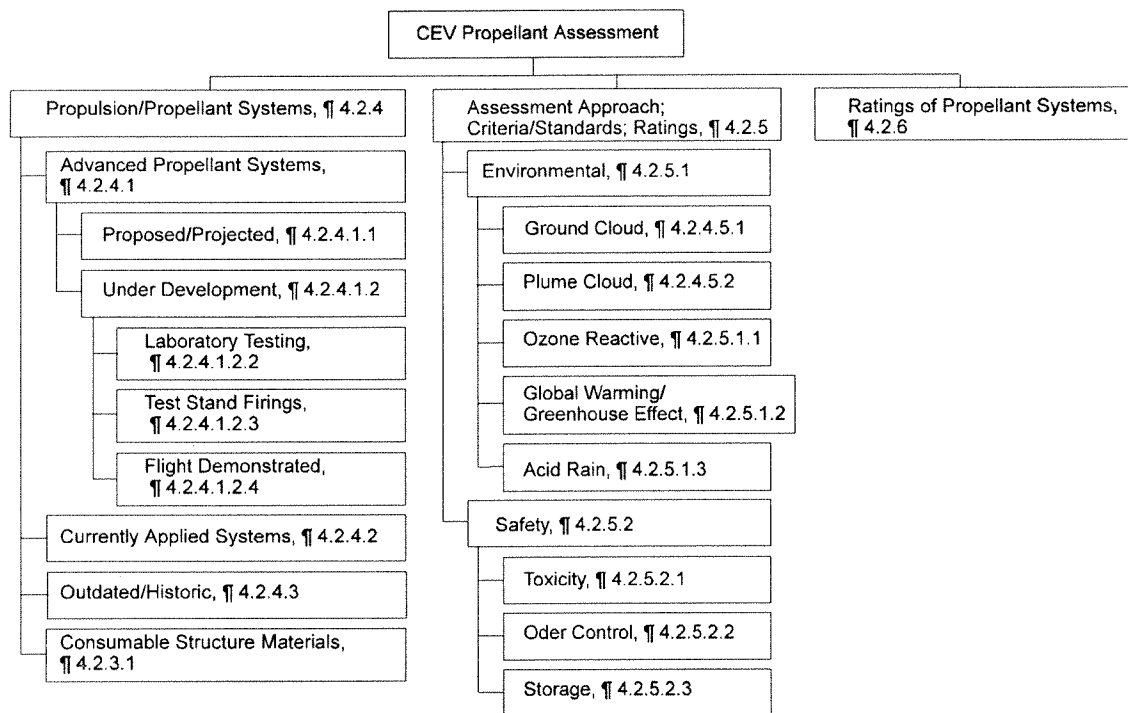


Figure 4.1-1 Propellant Assessment and Characterization Logic Chart

4.2. Technical Approach

4.2.1 Introduction and Background

Originally, strategic missiles, starting with the German V-2, Atlas, Titan 1, and Thor, and rocket powered airplanes, such as the Me-263 and X-15, used liquid propellant engines (Ref. 4-5). But the demand for instant readiness for the strategic missiles required solid propellants, and are currently used. Increased carrying capacity needs for liquid-powered vehicles has resulted in the use of strap-on solid propellant boosters, most notable on the SST (Space Shuttle), but also common on the Delta (upgraded Thor) and Ariane.

Increasing power output requirements (typically expressed as ΔV , I_{sp} , or density I_{sp}) have lead to continuing studies of 'improved' propellant combinations, for solids, liquids, hybrids (one component liquid, one solid), and gases. Suppression or reduction of detection of tactical and strategic missile launches and flight paths, typically performed by exhaust plume detection and analysis, is still causing efforts to reduce detectability by changing exhaust compositions from altering the propellant constitution or reactant ratios (smokeless propellants). Safety implications have resulted in the continuing effort to develop propellants with 'Reduced Sensitivity.' And recently, environmental concerns have focused efforts on application of propellant combinations that reduce emission of potentially environment-harmful species.

Significant factors in and causes of environmental degradation are 1). increased atmospheric transmission of solar ultraviolet radiation due to stratospheric ozone depletion and 2). global warming from increased atmospheric absorption of terrestrial infrared radiation by greenhouse gases in the atmosphere at all altitudes and from stratospheric mists. Federal and international priorities emphasize first the immediate elimination of human activity-caused ozone depletion, and second the near term elimination of human activity-caused greenhouse gas production.

Identified factors in ozone depletion include catalytic cycles involving ClO_x, BrO_x, HO_x, NO_x, (where x may be zero) and hydrated nitric acid in the form of a very low temperature ice. Except for monatomic and diatomic elemental species, all gases and vapors absorb in the infrared to a greater or less extent, and can cause retention of global heat. Sulfuric acid mist in the stratosphere also prevents escape of thermal infrared radiation.

4.2.2 Typical Propulsion System Application Categories

General applications for rocket-power in the operation of rocket-driven flight vehicles are included in the following list; this listing does not include rocket-powered devices such as JATO used on conventional aircraft.

- Main/Boost Propulsion (MBP).
- Boost Phase Attitude Control including TVC (BAC).
- Orbital Maneuvering/Station Keeping/Attitude Control (OAC).
- Reentry Initiation (RI).
- Rocket/Jet Powered Landing (RPL).
- Hot Gas Powered Mechanical Systems (HGP).

The list is not meant to be complete; igniters, destruct systems, and other brief-acting items are excluded because their effluent quantities are comparatively negligible. This latter exclusion does not apply to effluent release from combustion of the main propellant supply when a vehicle is destroyed on the command of the Range Officer.

Categories of system applications are numerous. For this report they will be limited to the following:

- Ground/Sea Launched, including
 - First (main) stage
 - Upper Stages
 - Strap-on
 - Single-stage to orbit
 - Space plane
- Air Launched
- Space/Orbit Launched
- Ground/Sea Launched Strategic
 - Strategic Testing
 - Reworked as Launch Vehicle
- Tactical
 - Ground/Sea Launched
 - Air Launched
 - Cruise Missile

4.2.3 Propellant Composition Categories

There are several types of categorizations commonly used to classify grouping of propellant systems. The most common is the physical state of the propellant while stored on the vehicle:

- Gas
- Liquid - cryogenic
 - storable
- Gelled Liquids - cryogenic
 - storable
- Liquid/Solid Hybrid
- Solid

Liquid propellant system chemical complexity is indicated by the categories:

- Monopropellant (oxidizer and fuel combined in one system)
 - Multi-constituent monopropellant
- Bipropellant (separate oxidizer and fuel flows)

Another level of categorization is based on whether or not spontaneous ignition invariably occurs when the propellants are brought into contact (this does not apply to solid propellants):

- Hypergolic (spontaneously ignites)
- Non-hypergolic
 - Non-hypergolic with slug hypergolic ignition

Constraints related to safety of personnel and protection from explosion hazards have introduced the NATO Insensitive Munitions Information Center (NIMIC) bifurcation:

- Sensitive
- Insensitive
 - High explosives
 - Munitions

Advances in detection technology have resulted in emphasis on hiding the flight path and launch point of armament rockets. Typically the categories are:

- Smoky propellants
- Low Smoke propellants / Reduced Signature propellants
- Smokeless propellants

These categories are also of considerable import in considering environmental atmospheric effects. Particulate emission is controlled by the EPA for health reasons, and can affect atmospheric transmission of infrared radiation; particulates such as Al_2O_3 and condensibles, such as H_2O are of concern in heterogeneous ozone depletion reactions, significant in the upper troposphere and stratosphere.

Development status of the propellant system can be used to distinguish among those systems that are routinely used on a significant scale from those that have been proposed or tested but are not currently applied on previous or current hardware:

- Advanced
 - Proposed/Projected

- Under Development
 - Laboratory Testing
 - Test stand firings
 - Flight demonstrated

- Currently Applied

- Old Technology /Outdated Systems (may be resurrected with use of stored hardware) e.g., for RSLP (Reentry Systems Launch Program)

Table 4.2.3-1 contains descriptions of some of the characteristics of current launch systems, and identifies many of the current applications. It has been modified from Reference 4-6 by inclusion of many U.S. Department of Defense vehicles. The U.S. DoD vehicles are included relative to peacetime launches, not wartime use. Non-U.S. strategic vehicles have not been added because of lack of information on retrofitting and launches for other purposes. NO_x has been added to the listing of all exhausts that contain N₂, representing afterburning.

Table 4.2.3-1 Characteristics of Propulsion Systems for Major Space Launch Vehicles

COUNTRY	APPLICATION	ENGINE/MOTOR	VACUUM THRUST (lbf)	PROPELLANT COMBINATION	MAJOR EXHAUST PRODUCTS
--	--	--	--	O ₂ /H ₂	H ₂ , H ₂ O
China	Long March	YF-73	9,900		
Europe	Ariane 4	HM7	14,000		
	Ariane 5	Vulcain	242,000		
USA	Centaur	RL10A-3-3A	16,500		
	STS	SSME	470,000		
	ALS, NLS	STME	580,000		
Japan	H-1, H-2	LE-5	25,000		
	H-2	LE-7	265,000		
CIS	Energia	RD-0120	441,000		
USA	Atlas	MA-5A Sustainer	84,400	O ₂ /RP-1	CO, CO ₂ , H ₂ , H ₂ O
		MA-5A	469,200		
	Delta	RS-27A	237,000		
Japan	N-2, H-1	MB-3	172,500		
CIS	Proton	RD-?	19,000		
	Energia	RD-170	444,200		

--	--	--	--	N ₂ O ₄ /Hydrazine	N ₂ , NO _x , H ₂ , H ₂ O
--	--	--	--	(Aerozine 50)	(CO ₂ , CO)
China	Long March	YF-22	162,000		
Europe	Ariane	Viking	170,000		
USA	Titan, Delta	AJ-10-118	9,700		
		N-2 (Japan)			
	Titan	LR-91	100,000		
	Titan	LR-87	548,000		
CIS	Proton	RD-?	135,000		
(Russia)	Proton	RD-235	368,000		

Table 4.2.3-1 (Continued)
Characteristics of Propulsion Systems
for Major Space Launch Vehicles

COUNTRY	APPLICATION	ENGINE/ MOTOR	VACUUM THRUST (lbf)	PROPELLANT COMBINATION	MAJOR EXHAUST PRODUCTS
--	--	--	--	Solid	HCl, Al ₂ O ₃ , CO ₂ , CO, N ₂ , H ₂ , H ₂ O, Nox (Metal oxides, others depending on specific composition.)
Europe	Ariane 4	P9.5	146,000		
	Ariane 5	EAP/MPS	1,433,000		
USA	STS	RSRM	5,400,000		
		ASRM			
	Titan 34D	UA 1205	2,400,000		
	Titan IV	UA 1207	1,600,000		
	Titan II	Castor	1,122,400		
	Atlas II AS	Castor 4A	394,000		
	Delta 6920	Castor 4A	929,400		
	Delta 7920	GEM	985,500		
	Minuteman I-III, Stage I	TU-122	218,000		
	Minuteman III, Stage II	SR-19-AJ-1	74,000		
	Minuteman III, Stage III	SR-73-AJ-1	41,900		
	Peacekeeper, Stage I	TU-903	595,200		
	Peacekeeper, Stage II	MGM-18A	338,900		
	Peacekeeper, Stage III	SR-120-HP-1	328,000		
	Polaris (Classified)				
	Poseidon (Classified)				
	Trident (Classified)				
--	--	--	--	Solid	HCl, Al ₂ O ₃ , CO ₂ , CO, N ₂ , H ₂ , H ₂ O, NOx
	ASROC	EX-114	12,600		
	Tartar	MK-27	16,200		
	Terrier	X-256	72,200		
	RSLP				
	Minuteman I&II, Stage I	(see above)	218,000		
	Minuteman I, Stage II	SR-19-AJ-1	50,000		
	Minuteman I, Stage III		22,000		
	Minuteman II, Stage II	M56-A1	50,300		
	Minuteman II, Stage III	XM-57	22,000		
	Talos	X251-C1	128,700		
	Sergeant	XM100	45,000		
	ORBUS				
Japan	N-2	Castor 2	468,000		
	H-1A	Castor 2	468,000		
	H-2	Nissan	46,200		
	MU-3S-2	M-13	283,000		
		SB-735	73,700		
		M-23	117,500		
		M-3B	29,700		
	M-5	M14	947,720		
		M24	308,560		
		M34	65,500		

4.2.3.1 Consumable Structural Materials (Ablatives, Liners, etc., Thrustors and Re-entry Vehicle Exteriors.)

An aspect of rocket propulsion exhaust composition is the contribution of combustible/ablative structural materials that react with propellant/exhaust constituents in the combustion chamber and/or the throat or nozzle. While the total mass reacted in a flight is very minor compared to the propellant quantities, they can introduce additional constituents and should be evaluated. Their contributions to the exhaust composition are typically ignored in rocket performance calculations because they have negligible effect on the thrust performance, although their production is considered when the ablative's protective or thermal performance is studied. They can produce environmentally active species.

Almost all solid propellant designs include an outer adhesive bonding layer, a case insulator and a liner. These are usually not involved in combustion of center-burning grains, (burn outward

from the center toward the case) except during burn termination. However they are involved in end-burning grains (cigarette burners.) The liners usually consist of the same constituents as the propellant resin, without the reactive fuel and oxidizer constituents (AP or Al.) Thus they do not introduce new constituents in the exhaust.

Ablative throats and nozzle liners can be reactants during all stages of combustion. Typical throats are made from mineral fiber-resin composites and can produce/introduce additional metal-oxide particles, such as SiO_2 from fiberglass. Ablative throats may also be impregnated metals, where the impregnation may be a relatively volatile metal such as silver. Typical non-ablative nozzle liners consist of oxidation-resistant refractory metals that resist significant reaction with the exhaust gases.

Thermal protection for re-entry can also introduce additional species, but these are not included in this study of rocket propellant chemistries.

This mention of additional constituents is included for completeness. It is beyond the scope of the current contract to review the data from materials development test firings to collect the data and integrate them into the exhaust composition of currently used vehicles.

4.2.4 Propellant Compositions by Physical Categories

There are myriad chemical combinations that have been proposed and applied for rocket propulsion, far too many for consideration of all of them in this report. A selection has been made of those in use and those judged most likely for large scale application in the next decade; these are tabulated in the appropriate categories below. The categories found useful to group propellant systems, a subset of those listed in Section 4.2.3, are grouped in Table 4.2.4-1.

Table 4.2.4-1 Significant Propellant System Categories

Propellant System Physical State	Combustion Category	Special Characteristics
Gas	Monopropellant	Hot Gas
Gas	Bipropellant	
Liquid	Monopropellant	Single Active Constituent
Liquid	Monopropellant	Multi Constituent
Liquid	Monopropellant	TVC Injectants
Liquid	Bipropellant	non-hypergolic
Liquid	Bipropellant	Hypergolic
Liquid	Tripropellant	Heavy Lift Vehicle
Gelled Liquid	Monopropellant	
Gelled Liquid	Bipropellant	Hypergolic
Gelled Liquid	Bipropellant	Hypergolic, Low Smoke
Liquid - Slush	Bipropellant	non-hypergolic
Liquid/Solid Hybrid	Bipropellant	non-Hypergolic
Liquid/Solid Hybrid	Bipropellant	Hypergolic
Solid	Monopropellant	non-Hypergolic
Solid	Conventional Solid	non-Hypergolic
Solid	Reduced Smoke	non-Hypergolic
Solid	H, C, O, and Cl free	non-Hypergolic
Solid	Chlorine-free exhaust	non-Hypergolic
Solid	HCl free exhaust	non-Hypergolic
Solid	Neutralized HCl	non-Hypergolic
Solid	Scavenged HCl	non-Hypergolic
Solid	Decreased HCl	non-Hypergolic

4.2.4.1 Advanced Propellant Systems

Research, development, and application of new propellant systems is a continuing process. Improved specific impulse, (I_{sp}), alone and in combination with additional objectives including safety, compatibility, combustion control, reduced detectability (signature), have more recently been coupled with control and reduction of undesirable environmental consequences. The new systems range from modifications to current systems to completely new chemical combinations; of course the changes target both conventional liquid and solid propellants and advanced concepts such as hybrids, gels, and slush cryogens.

A serious issue is arising from efforts originally instigated to reduce exhaust plume signature and addressed more recently to control ground cloud formation/exhaust toxicity by eliminating the formation and emission of Al_2O_3 solids that occur from most solid propellants and some gelled hypergolic liquids. Aluminum powder was originally added to fuel compositions to attain improved propellant density and to also produce higher flame temperature and greater energy (thrust). But a very important additional benefit quickly became apparent; this new benefit is the control and decrease of acoustic wave/combustion instability. Control is by the 'snowstorm' of very fine (0-20

μm) particles of alumina, which cause 'particle damping' of the acoustic waves (increased decay rate of peak pressure amplitude).

Combustion instability is a significant phenomenon that has been addressed at SPIA and CPIA JANNAF Combustion Meetings for many years; see, for example, the 13 technical papers in Ref. 4-7. In this group, the paper by Derr, Ref. 4-8, is a clear explanation of the instability-reduction phenomena. See also the comment by E. W. Price in his summary report on a workshop about Aluminum Powder Combustion, "The principle impetus to study the behavior has been its overwhelming effect on combustion stability.", Ref. 4-9.

Experimental substitution of other oxides in the exhaust, such as B₂O₃ or MgO, does not provide sufficient damping (Ref. 4-10).

Interpretation of the data indicates that new, exhaust particulate-free anti-combustion instability approaches MUST be developed, proven, and implemented before instituting measures to remove Al₂O₃ from exhausts.

Combustion stability studies of aluminum-loaded gelled propellants have not been found.

Afterburning suppression approaches are based on reducing the temperature of the exhaust. This can be accomplished by: 1) decreasing the O/F ratio (applies to all propellants) and; 2) by incorporation of small amounts of coolant additives to gels, hybrids, and solids, see Table 4.2.4-2.

Table 4.2.4-2 Candidate Afterburning Suppression Additives

Additive Name	Additive Formula	Concentration mole %
Sodium chloride	NaCl	0.065
Potassium fluoride	KF	0.048
Potassium chloride	KCl	0.031
Potassium iodide	KI	0.056
Potassium sulfate	K ₂ SO ₄	0.036

All the candidates unfortunately add particulates to the plume, and except for KF probably consume stratospheric ozone and contribute to Global Warming.

4.2.4.1.1 Proposed/Projected

Advanced propellant approaches that exist only as theoretical studies and proposed approaches are not widely reported because they are generally regarded as proprietary by the originators. Sketchy information becomes available after actual laboratory testing and development starts; the more developed and attractive the system, the more detailed the data, see Table 4.2.4-3, in which combustion products are listed in order of decreasing quantity. On the other hand, security restrictions prevent general release of data on important applied systems used in weapons.

Exhaust products are listed with each composition; these include some species due to afterburning, added for this report. However, quantization of exhaust plume composition subsequent to afterburning, while well within the capabilities of available chemical analysis tools and of combustion-model computer programs, is infrequently performed and seldom published.

Table 4.2.4-3 Proposed/Projected Advanced Propellant Systems

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton		
Liquid	Heavy Lift Vehicle Tripropellant	LO ₂ + [LH ₂ + CH ₄ / RP-1] (Ref. 4-11)	H ₂ O;	81.0	1814
			CO ₂ ;	14.0	314
			CO;	4.5	101
			H ₂ ;	0.1	2
			NO _x ;		
Gelled Liquids	Hypergolic Bipropellants	F ₂ (gel) + N ₂ H ₄ (gel) (Vanadium fluoride candidate gelling agent for LF ₂)	HF;	73.0	1635
			N ₂ ;	26.9	603
			VF ₅ ;	0.03	0.6
			CO;	0.03	0.6
			CF ₄ ;	0.02	0.4
			NO _x ;		
		Gel F ₂ + Gel H ₂	HF;	78.5	1758
			F;	20.1	450
			H ₂ ;	0.3	6.7
			H;	0.1	2.2
			CF ₄ ;	0.03	0.7
			VF ₅ ;	0.03	0.7
			CO;	0.02	0.4
		Gel F ₂ + Gel NH ₃	HF;	80.2	1796
			N ₂ ;	19.7	441
			CO;	0.03	0.7
			VF ₅ ;	0.03	0.7
			CF ₄ ;	0.02	0.4
			NO _x ;		
Liquid/Solid Hybrid	non-Hypergolic Bipropellant	LO ₂ + Butyl rubber	CO;	44.5	997
			CO ₂ ;	33.6	753
			H ₂ O;	20.2	452
			H ₂ ;	1.0	22
			N;	0.4	9
			OH;	0.03	1
			NO _x ;		

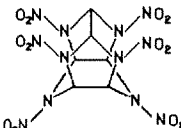
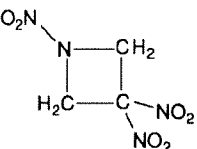
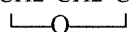
4.2.4.1.2 Under Development

4.2.4.1.2.1 Advanced Energetic Materials

New types of energetic materials, suitable for use as explosives and as solid propellant chlorine-free, higher energy, oxidizer ingredients, have been demonstrated lately. A number of them are based on or consist of nitramine compounds. Others are “energetic” polymers, that are not only fuel-binders but actually supply additional energy during combustion, similar to the now-abandoned polymers containing -NF₂ groups. Most of the work on these new ingredients, including propellant

performance, is classified. Table 4.2.4-4 is a summary of the chemical identities of some of the advanced energetic materials.

Table 4.2.4-4 Advanced Energetic Materials Identification (Ref. 4-12)

Chemical Name	Code or Acronym	Structure or Formula	Notes
Ammonium dinitramide	ADN	$\text{NH}_4\text{N}(\text{NO}_2)_2$	Explosive. Anticipated use: Solid propellant oxidizer; chlorine free
Potassium dinitramide	KDN	$\text{KN}(\text{NO}_2)_2$	Anticipated use: Energetic phase stabilizer for AN
Potassium dinitramide phase-stabilized ammonium nitrate, cocrystallized	KDN-AN	$\text{KN}(\text{NO}_2)_2$ "few" % + NH_4NO_3	Explosive. Anticipated use: Solid propellant oxidizer, environmentally conscientious
Hexanitrohexaaza <i>isowurtzitane</i>	CL-20		Explosive. Anticipated use: Solid propellant oxidizer, minimum signature
1,3,3-Trinitroazetidine	TNAZ		Explosive. Anticipated use: Solid propellant oxidizer, minimum signature
Glycidyl azide polymer	GAP	see Table 4.2.4-6	Solid propellant oxidizer, minimum signature
Oxetane polymers; Bisazidomethyloxetane Azidomethylmethyl-oxetane Nitramethylmethyl-oxetane	BAMO, AMMO, NMMO	Oxetane is $\text{CH}_2\text{-CH}_2\text{-CH}_2$  see Figure 4.2.4.2-1	Energetic binders

The JANNAF Interagency Propulsion Committee has released a call for papers for an April confidential meeting about new energetic materials, Ref. 4-13. The specific technical topics are to include CL-20 and ADN, and the improved fuel, exploded aluminum (code ALEX).

4.2.4.1.2.2 Laboratory Testing

Information on propellants still in the initial chemical laboratory investigation stage is mostly limited to liquid systems, see Table 4.2.4-5. Elemental liquid fluorine and fluorine-oxygen mixtures (FLOX) are no longer considered as serious contenders because of perceived handling safety constraints, even though they have superior I_{sp} .

Table 4.2.4-5 Advanced Propellant Systems Under Development; Laboratory Testing

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton	
Liquid	Bipropellants	$N_2H_4 + N_2F_4$	HF;	57.6 1290
			N_2 ;	42.4 950
			NOx;	
		$N_2H_4 + ClF_5$	HF;	54.8 1228
			N_2 ;	24.2 542
			HCl;	21.0 470
			NOx;	
		$B_2H_6 + OF_2$	BF_3 ;	35.6 797
			HF;	31.0 694
			B_2O_3 ;	19.0 426
			H_2O ;	14.7 329
		$C_2H_4 + OF_2$	HF;	67.8 1519
			CF_4 ;	18.8 421
			CO;	5.5 123
			CO_2 ;	5.9 132
			H_2O ;	2.1 47
Solid	H, C, O, and Cl free	$NF_4BF_4 + Li$ or B + Poly PNF ₂	H_2 ;	3.4 76
			H_2O ;	96.6 2164
			PF_5 ;	62.0 1389
			N_2 ;	11.5 258
			$LiBF_4$;	15.4 345
			BF_3 ;	11.1 249
			NOx;	
			PN;	
			BN;	

4.2.4.1.2.3 Test Stand Firings

Information about many more propellant systems becomes available when the technology reaches this level, including new solid propellant formulations. Unfortunately, published combustion product compositions seldom include the contributions from low level additives (catalysts, stabilizers, etc.) that often add metals and metal oxides at federally reportable-controlled levels to the plume.

Full up combustion calculations typically include them in the calculated output, but they are not reported since they do not significantly affect the thrust and in some cases would reveal

proprietary details. All the additives included are typically not reported in the published formulations, so other investigators are not able to fill the deficiencies. These details do become known for actual applied systems, especially for defense applications, in the CPIA propellant manuals (Ref. 4-14) Unfortunately, because much of the data in the Solids manual is classified, access is restricted to individuals with security clearances.

Propellant systems at this stage of development, see Table 4.2.4-6 have passed a number of reviews and are poised for application to actual vehicles. It now becomes a matter of demonstrating system tradeoffs for potential benefits and costs of the advanced approach against the known characteristics of current systems. Environmental interactions are becoming of significant impact at this appraisal.

Table 4.2.4-6 Advanced Propellant Systems Under Development; Test Stand Firings

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton
Gas	Monopropellants <u>Hot Gas</u> (Arcjet, Resistojet/ Ion Propulsion)	H ₂	H ₂ ; 100 2240
		NH ₃	N ₂ ; 82.4 1846
			H ₂ ; 17.6 394
			NOx;
Gas (Cont.)	Monopropellants Hot Gas	Xe	Xe; 100 2240
		Li	Li; 100 2240
Liquids	Hypergolic Bipropellants	LF ₂ + LH ₂	HF; F; 78.6 1761
			H ₂ ; 20.1 450
			H; 0.3 7
			0.1 2
Gelled Liquids	Hypergolic	N ₂ H ₄ + IRFNA (with gelling solids)	H ₂ ;
			H ₂ O;
			Li ₂ O;
			CO;
			CO ₂ ;
			SiO ₂ ;
			N ₂ ;
			NOx;
	Hypergolic, Low Smoke	N ₂ H ₄ + IRFNA (with low smoke gelling solids)	H ₂ ;
			H ₂ O;
			CO;
			CO ₂ ;
			N ₂ ;
			NOx;

Table 4.2.4-6 (Cont.)
Advanced Propellant Systems Under Development; Test Stand Firings

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton
Liquid/Solid Hybrid	Hypergolic	$\text{LiBH}_4 + (9 \text{ H}_2\text{O}_2 + 1 \text{ H}_2\text{O})$	$\text{H}_2\text{O};$ 76.8 1720 $\text{Li}_2\text{O};$ 5.9 132 $\text{B}_2\text{O}_3;$ 17.2 385 $\text{H}_2;$
Solid	Chloride-free exhaust	GAP (Glycidyl Azide Polymer) + TMETN (Trimethylolethane trinitrate) + AN (NH_4NO_3)	$\text{H}_2\text{O};$ $\text{CO};$ $\text{CO}_2;$ $\text{N}_2;$ $\text{H}_2;$ $\text{NOx};$
<p>The structure of GAP reported in Ref. 4-15 is</p> $\text{HO}-[\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}]_n-\text{CH}_2-\text{CH}_2-\text{O}-[\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}]_n-\text{H}$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \\ \text{CH}_2\text{N}_3 \end{array}$ </div> <div style="text-align: center;"> $\begin{array}{c} \\ \text{CH}_2\text{N}_3 \end{array}$ </div> </div> <p>which has an equivalent weight of 1192</p>			
Solid (Cont.)	HCl free	PGA + TEGDN + ZnO Phase-Stabilized AN + MgAl HTPE + BuNENA + Amine phase-stabilized AN + MgAl	$\text{CO};$ $\text{CO}_2;$ $\text{H}_2;$ $\text{H}_2\text{O};$ $\text{N}_2;$ $\text{NOx};$ $\text{MgO};$ $\text{Al}_2\text{O}_3;$ $\text{CO};$ $\text{CO}_2;$ $\text{H}_2;$ $\text{H}_2\text{O};$ $\text{N}_2;$ $\text{NOx};$ $\text{MgO};$ $\text{Al}_2\text{O}_3;$
		HAN/AN + Al + PVA	$\text{CO};$ $\text{CO}_2;$ $\text{H}_2;$ $\text{H}_2\text{O};$ $\text{N}_2;$ $\text{NOx};$ $\text{Al}_2\text{O}_3;$

Table 4.2.4-6 (Cont.)
Advanced Propellant Systems Under Development; Test Stand Firings

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton
Solid (Cont.)	Neutralized HCl	HTPE + AN + AN + MgAl	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; MgO; Al ₂ O ₃ ; MgCl ₂ ;
	Scavenged HCl	HTPB + DOA + Al + NaNO ₃ + AP + 0.8% KP	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; NaCl; KCl; Na ₂ O; K ₂ O; NaOH; KOH;
	Scavenged HCl	HTPB + AP + NaNO ₃ + HMX + Al	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; NaCl; Na ₂ O; NaOH;
Solid (Cont.)	Decreased HCl	AP, Al, CTPB, BITA, Polybutene, HAN, PVA	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; HCl;

2 45

4.2.4.1.2.4 Flight Demonstrated

There are only a few advanced systems in this stage of development, see Table 4.2.4-7.

A calculated performance comparison of neat hydrazine with a range of compositions of alumizine is presented in Figure 4.2.4.1-1. Calculated performances for several of the advanced and conventional liquid propellants at a range of O/F weight ratios are compared in Figure 4.2.4.1-2.

Table 4.2.4-7 Advanced Propellant Systems Under Development; Flight Demonstrated

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton
Gas	Bipropellant Systems	H ₂ +O ₂ (ACS: MD/X Single-Stage to Orbit Subscale Test Vehicle)	H ₂ O; 96.6 2164
			H ₂ ; 3.4 76
Liquid	Gelled Liquid Monopropellant	Alumizine (Al-gelled hydrazine)	H ₂ ; N ₂ ; NH ₃ ; AlN; Al ₂ O ₃ ; NO _x ; H ₂ O;

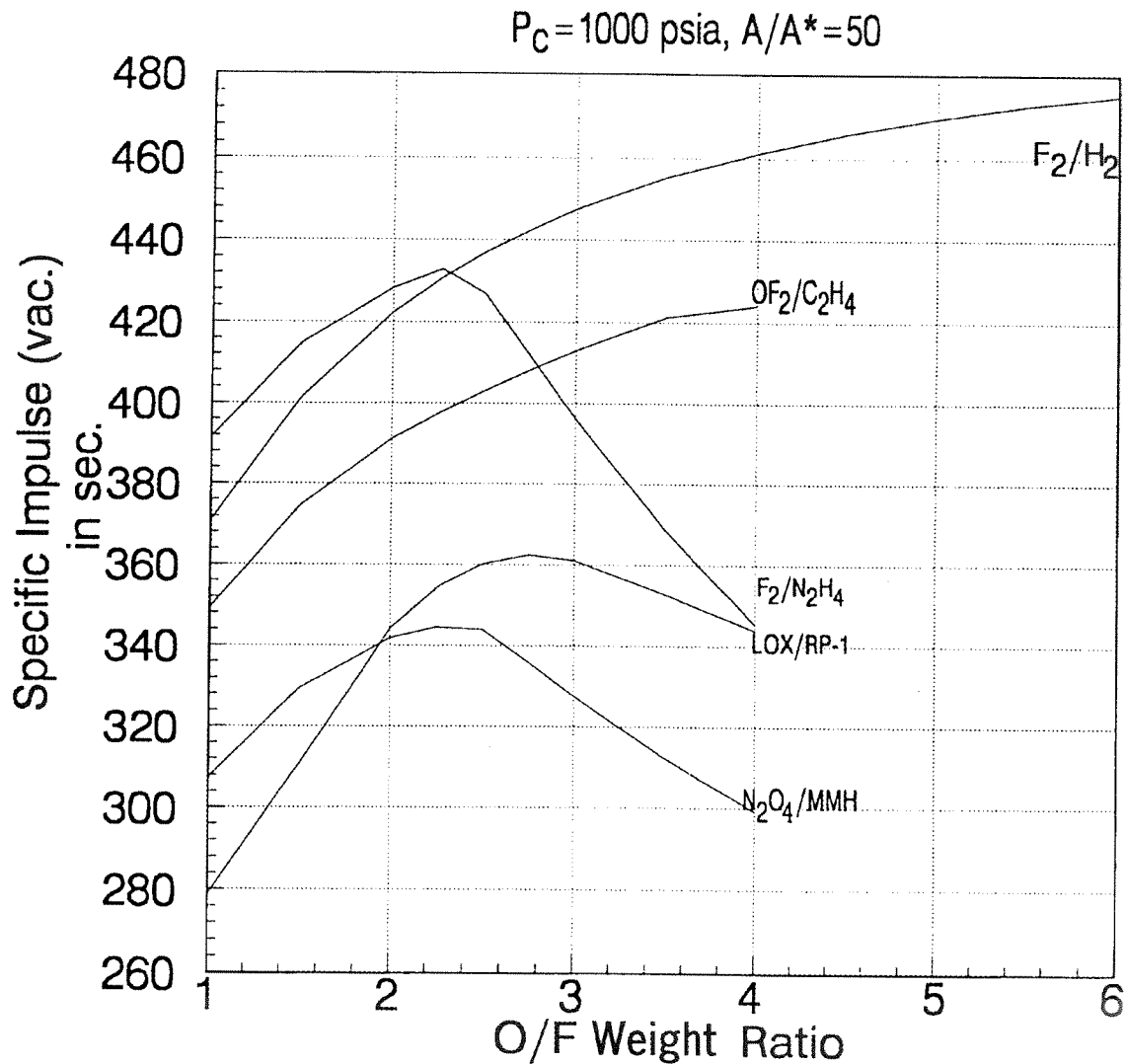


Figure 4.2.4 Effect of O/F Weight Ratio on Propellant Performance

4.2.4.2 Currently Applied Propellant Systems

Table 4.2.4-8 consists of lists of propellant ingredients and exhaust compositions for the majority of propellant systems that are used primarily for launch and boost systems, currently and planned for the near future; it does not contain data from small scale tactical arms.

Table 4.2.4-8 Currently Applied Propellant Systems

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton	
Gas	Monopropellants	H ₂	H ₂ ;	100 2240
		N ₂	N ₂ ;	100 2240
Liquid	Single Active Constituent Monopropellants	N ₂ H ₄	N ₂ ;	
			H ₂ ;	
			NH ₃ ;	
			H ₂ O;	
			NO _x ;	
		9 H ₂ O ₂ + 1 Water	H ₂ O;	55.6 1245
			O ₂ ;	44.4 995
		Ethylene Oxide	H ₂ ;	37.2 833
			CO;	18.6 417
			CH ₄ ;	7.0 157
			H ₂ O;	6.0 134
			CO ₂ ;	2.2 49
			C ₂ H ₄ ;	
			O ₂ ;	
		Nitromethane	CO;	38.2 8564
			H ₂ O;	24.6 551
			N ₂ ;	22.0 93
			CO ₂ ;	12.1 271
			H ₂ ;	2.2 49
			CH ₂ O;	
			NO _x ;	
		<i>n</i> -Propyl Nitrate	CO;	53.8 1205
			H ₂ ;	9.6 215
			N ₂ ;	6.9 155
			CO ₂ ;	5.8 130
			H ₂ O;	5.8 130
			CH ₄ ;	5.5 123
			C;	1.7 38
			NO _x ;	

Cont.

**Table 4.2.4-8 (Cont.)
Currently Applied Propellant Systems**

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton		
Liquid (Cont.)	Single Active Constituent Monopropellants (Cont.)	9 HAN (Hydroxyl ammonium nitrate)- 1 Water	H ₂ O; O ₂ ; NO _x ; NH ₃ ; N ₂ ;	38.8 32.7 28.6	869 732 641
	TVC Injectants	Freon 114B2 (Halon 2402) C ₂ F ₄ Br ₂ FC-40 (polychlorotri-fluoroethylene fluid) Perfluorohexane Sr(ClO ₄) ₂ -Water	C ₂ F ₄ Br ₂ ; C ₂ ClF ₃ ; C ₆ F ₁₄ ; SrO; HCl; H ₂ O; O ₂ (probably consumed to CO, CO ₂);	100 100 100	2240 2240 2240
	Multi Constituent Monopropellants	Dinitroxypropane-dibutyl sebacate-2-nitrodiphenylamine (Otto fuel II) Diethyleneglycol dinitrate-trimethylolethane trinitrate-triethyleneglycol dinitrate Hydroxylammonium perchlorate-dioxane-water (NOS-58-6)	CO; CO ₂ ; H ₂ O; N ₂ ; NO _x ; CO; CO ₂ ; H ₂ O; N ₂ ; NO _x ;		
	Bipropellant Systems				
	Non-hypergolic (slug hypergolic ignition ignored)	H ₂ + O ₂ CH ₄ + O ₂	H ₂ O; H ₂ ; H ₂ ; H ₂ O; CO; CO ₂ ;	96.6 3.4	2164 76

Cont.

**Table 4.2.4-8 (Cont.)
Currently Applied Propellant Systems**

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton	
Liquid (Cont.)	Non-hypergolic(Cont.)	NH ₃ + O ₂	H ₂ ;	
			H ₂ O;	
			N ₂ ;	
			NO _x ;	
		RP-1 + O ₂	CO;	49.7 1113
			H ₂ O;	24.1 540
			CO ₂ ;	20.9 468
			OH;	2.6 58
			H ₂ ;	1.1 25
			O ₂ ;	0.9 20
			O;	0.5 11
			H;	0.2 4
		N ₂ H ₄ + O ₂	N ₂ ;	
			NH ₃ ;	
			H ₂ ;	
			H ₂ O;	
			NO _x ;	
		UDMH + O ₂	CO;	
			CO ₂ ;	
			N ₂ ;	
			NH ₃ ;	
			H ₂ ;	
			H ₂ O;	
			NO _x ;	
		N ₂ H ₄ + MON (mixed oxides of nitrogen)/ IRFNA	H ₂ ;	
			H ₂ O;	
			N ₂ ;	
			NO _x ;	
		MMH + MON/IRFNA	CO;	
			CO ₂ ;	
			N ₂ ;	
			NH ₃ ;	
			H ₂ ;	
			H ₂ O;	
			NO _x ;	

Cont.

**Table 4.2.4-8 (Cont.)
Currently Applied Propellant Systems**

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton		
Liquid (Cont.)	Non-hypergolic(Cont.)	A-50(MMH AND UDMH)+ MON/IRFNA	CO; CO ₂ ; N ₂ ; NH ₃ ; H ₂ ; H ₂ O; NOx;		
Solid	Monopropellants	NaN ₃	N ₂ ; Na; Na ₂ O; NOx; NaOH;		
	Conventional Solids	Double Base	CO ₂ ;	27.7	620
			H ₂ O;	26.2	587
			CO;	23.4	524
			N ₂ ;	15.1	338
			H ₂ ;	7.6	170
		Double Base, Al, AP	Al ₂ O ₃ ;	30.4	681
			CO;	24.3	544
			HCl;	21.3	477
			H ₂ O;	9.6	215
				8.8	197
			N ₂ ;	3.6	81
			CO ₂ ;	2.1	47
			H ₂ ;	0.03	0.7
			H;	0.03	0.7
			OH;		
		Vinyl Polyester, 80% AP	H ₂ O;	48.2	1080
			HCl;	20.8	466
			CO ₂ ;	20.5	459
			N ₂ ;	10.4	233
			CO;	0.1	2
			H ₂ ;	0.1	2
			Cr ₂ O ₃ ;	0.03	0.7
			CrO ₂ ;	0.03	0.7

Cont.

**Table 4.2.4-8 (Cont.)
Currently Applied Propellant Systems**

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton		
Solid (Cont.)	Conventional Solids (Cont.)	Polysulfide, AP	H ₂ O;	41.5	930
			HCl;	18.4	412
			CO ₂ ;	13.7	307
			N ₂ ;	9.2	206
			H ₂ ;	4.0	90
			CO;	3.9	87
			H ₂ S;	2.6	58
			S ₂ ;	2.0	45
			SO ₂ ;	1.6	36
			HS;	0.03	0.7
			S;	0.02	0.4
		Polyurethane, AP, KP	CO ₂ ;	27.9	625
			H ₂ O;	24.9	558
			CO;	9.6	215
			N ₂ ;	8.6	193
			KCl;	6.6	148
			H ₂ ;	0.8	18
			CuO;	0.02	0.4
			Cr ₂ O ₃ ;	0.02	0.4
		Al, Polyurethane, AP	H ₂ ;	38.4	860
			CO;	28.7	643
			HCl;	12.0	269
			H ₂ O;	6.6	148
			Al ₂ O ₃ ;	6.5	146
			Al ₂ O ₃ ;	6.4	143
			N ₂ ;	1.3	29
			CO ₂ ;	0.1	2
			Cu;		
		Asphalt, KP (JATO only)	CO;	44.0	986
			H ₂ ;	27.4	614
			KCl;	15.1	338
			H ₂ O;	9.9	222
			CO ₂ ;	3.3	74
			SO ₂ ;	0.2	4
			N ₂ ;	0.1	2
		Rubber, AN (JATO only)	H ₂ O;	31.5	706
			H ₂ ;	28.6	641
			N ₂ ;	21.8	488
			CO ₂ ;	15.6	349
			CO;	2.5	56

Cont.

**Table 4.2.4-8 (Cont.)
Currently Applied Propellant Systems**

Physical Category	Application	Propellant Constituents	Nominal Exhaust, %w/w, lb/ton
Solid (Cont.)	Reduced Smoke	AP, HTPB, IPDI, DOA, Al, HX-752	CO; CO ₂ ; H ₂ O; HCl; Al ₂ O ₃ ; H ₂ ; N ₂ ;

Representative composition data for typical solid propellants, mostly for current systems, are tabulated on the following pages. The general functional characteristics of typical compositions are presented in Table 4.2.4-9. Representative compositions of the three commonest categories are listed in Table 4.2.4-10. More detailed nominal compositions for Double Base and Composite Modified Double Base are summarized in Table 4.2.4-11, and for Composite Solids in Table 4.2.4-12. Table 4.2.4-13 shows typical binder, plasticizer, and oxidizer/fuel selections for particular missions and experimental development of advanced propellants, especially reduced signature/smoke. These tables are copied from tables in Reference 4-16, some have been modified with additional data.

Estimated/typical weights of individual exhaust species per 100,000 lbf of thrust from the main classes of launch vehicles are presented in Table 4.2.4-14.

Table 4.2.4-9 Characteristics of Some Operational Solid Propellants

Propellant	I_{sp} Range	Flame Temperature	Density	Metal Content	Burning Rate ^c	Pressure Exponent	DoD Hazard
Type ^a	(sec) ^b	(°F)	(lb/in ³)	(% w/w)	(in/s)	n	Class ^d
DB	220-230	4100	0.058	0	0.45	0.30	1.1 or 1.3
DB/AP/Al	260-265	6500	0.065	20-21	0.78	0.40	1.3
DB/AP- HMX/Al	265-270	6700	0.065	20	0.55	0.49	1.1
NEPE/AP/Al	240-300	4500-4850	0.061- 0.066	0-20	0.02-0.50	0.30-0.62	1.1
PVC/AP/Al	260-265	5600	0.064	21	0.45	0.35	1.3
PS/AP/Al	240-250	5000	0.062	3	0.31	0.33	1.3
PU/AP/Al	260-265	5400-6000	0.064	16-20	0.27	0.15	1.3
PBAN/AP/Al	260-263	5800	0.064	16	0.55	0.33	1.3
CTPB/AP/Al	260-265	5600-5800	0.004	15-17	0.45	0.40	1.3
HTPB/AP/Al	260-265	5600-5800	0.067	4-17	0.40	0.40	1.3
PBAA/AP/Al	260-265	5400-6000	0.064	14	0.32	0.35	1.3
AN/Polymer	180-190	2300	0.053	0	0.3	0.60	1.3

^a Al, aluminum; AN, ammonium nitrate; AP, ammonium perchlorate; CTPB, carboxy-terminated polybutadiene; DB, double base, typically NC and NG; HMX, cyclotetramethylene tetranitramine; HTPB, hydroxy-terminated polybutadiene; PBAA, polybutadiene acrylic acid polymer; PBAN, polybutadiene acrylic acid acrylonitrile terpolymer; PS, polysulfide; PU, polyurethane; PVC, polyvinyl chloride; NEPE, nitrate ester polyether.

^b At 1000 psia expanding to 14.7 psia.

^c At 1000 psia.

^d Ref. 4-17.

Table 4.2.4-10 Representative Propellant Formulations

Double-Base (JPN Propellant)		Composite (PBAN Propellant)		Composite Double-Base (CMDB Propellant)	
Ingredient	Wt %	Ingredient	Wt %	Ingredient	Wt %
Nitrocellulose	51.5	Ammonium perchlorate	70.0	Ammonium perchlorate	20.4
Nitroglycerin	43.0	Aluminum powder	16.0	Aluminum powder	21.1
Diethyl phthalate	3.2	Polybutadiene-acrylic acid-acrylonitrile	11.78	Nitrocellulose	21.9
Ethyl centralite	1.0	Epoxy curative	2.22	Nitroglycerin	29.0
Potassium sulfate	1.2			Triacetin	5.1
Carbon black	<1.0			Stabilizers	2.5
Candelila wax	<1.0				

Source: Air Force Phillips Laboratory, Edwards, California.

Table 4.2.4-11 Typical Ingredients of Double Base (DB) Propellants and Composite Modified Double Base (CMDB) Propellants

Type	Percent	Acronym	Typical Chemicals
Binder	30-50	NC	Nitrocellulose (solid), usually plasticized with 20 to 50 % nitroglycerine
Reactive Plasticizer (liquid explosive)	20-50	{ NG DEGDN TEGDN PDN TMETN	Nitroglycerine Diethylene glycol dinitrate Triethylene glycol dinitrate Propanediol dinitrate Trimethylolthane trinitrate
Plasticizer (organic liquid fuel)	0-10	{ DEP TA DMP EC DBP	Diethyl phthalate Triacetin Dimethyl phthalate Ethyl centralite Dibutyl phthalate
Burn rate modifiers	UP TO 3	{ PbSa PbSt CuSa CuSt	Lead salicylate Lead stearate Copper salicylate Copper stearate
Coolant		OXM	Oxamine
Opacifier		C	Carbon black (powder)
Stabilizer and or antioxidant	>1	{ EC DPA	Ethyl centralite Diphenyl amine
Visible flame suppressant	up to 2	{ KNO ₃ K ₂ SO ₄	Potassium nitrate Potassium sulfate
Lubricant (for extruded propellant only)	> 0.3	{ C	Graphite Wax
Metal fuel	0-15	Al	Aluminum, fine powder (solid)
Crystalline oxidizer	0-15	{ AP AN	Ammonium perchlorate Ammonium nitrate
Solid explosive crystals	0-20	{ HMX RDX NQ	Cyclotetramethylenetetranitramine Cyclotrimethylenetrinitramine Nitroguanidine

Table 4.2.4-12 Typical Ingredients of Composite Solid Propellants

Type	Percent	Acronym	Typical Chemicals
Oxidizers (crystalline)	0-70	<div> <div>AP</div> <div>AN</div> <div>KP</div> <div>KN</div> <div>NP</div> </div>	<div>Ammonium perchlorate</div> <div>Ammonium nitrate</div> <div>Potassium perchlorate</div> <div>Potassium nitrate</div> <div>Nitronium perchlorate (experimental propellant only)</div>
Metal fuels (also act as a combustion stabilizer)	0-30	<div> <div>Al</div> <div>Be</div> <div>Zr</div> </div>	<div>Aluminum</div> <div>Beryllium (experimental propellant only)</div> <div>Zirconium (also acts as burn rate modifier)</div>
Fuel/Binder polybutadiene type	5-18	<div> <div>HTPB</div> <div>CTPB</div> <div>PBNA</div> <div>PBAA</div> </div>	<div>Hydroxyl-terminated polybutadiene</div> <div>Carboxyl-terminated polybutadiene</div> <div>Polybutadiene acrylonitrile acrylic acid</div> <div>Polybutadiene acrylic acid</div>
Fuel/Binder polyether or polyester type	0-15	<div> <div>PEG</div> <div>PAD</div> <div>PCB</div> <div>PGA</div> <div>PPG</div> <div>PU</div> </div>	<div>Polyethylene glycol</div> <div>Polyalkylene oxide</div> <div>Polycaprolactonepolyol</div> <div>Polyglycol adipate</div> <div>Polypropylene glycol \</div> <div>Polyurethane polyester or polyether</div>
Fuel/Binder other	0-20	PVC	<div>Polysulfide</div> <div>Polyvinyl chloride</div>
Curing agents or cross-linkers that react with polymer binder	1-3.5	<div> <div>MAPO</div> <div>BISA</div> <div>IPDI</div> <div>TDI</div> <div>HMDI</div> <div>DDI</div> <div>TMP</div> <div>BITA</div> </div>	<div>Methyl aziridinyl phosphine oxide Butylene imine adduct of <i>isosebacic acid</i> Isophorone <i>diisocyanate</i></div> <div>Toluene-2,4-<i>diisocyanate</i></div> <div>Hexamethyl <i>diisocyanate</i></div> <div>Dimethyl <i>diisocyanate</i></div> <div>Trimethylol propane</div> <div>Trimesoyl-1(2-ethyl)-aziridine</div>
Explosive fillers (solid)	0-40	<div> <div>HMX</div> <div>RDX</div> <div>NQ</div> </div>	<div>Cyclotetramethylenetetranitramine</div> <div>Cyclotrimethylenetrinitramine</div> <div>Nitroguanadine</div>
Plasticizer/Pot life control (organic liquid)	0-7	<div> <div>DOP</div> <div>DOA</div> <div>DOS</div> <div>DMP</div> <div>DMA</div> <div>IDP</div> <div>Oronite 6</div> </div>	<div>Dioctyl phthalate (octyl = 2-ethylhexyl)</div> <div>Dioctyl adipate</div> <div>Dioctyl sebacate</div> <div>Dimethyl sebacate</div> <div>Dimethyl adipate</div> <div><i>Isodecyl pelargonate</i></div> <div>Dibutyl carbitol</div> <div>Circo light oil</div> <div>Polybutene</div>
Energetic plasticizers (liquid)	0-14	<div> <div>GAP</div> <div>NG</div> <div>DEGN</div> <div>BTTN</div> <div>TEGDN</div> </div>	<div>Glycidyl azide polymer</div> <div>Nitroglycerine</div> <div>Diethylene glycol dinitrate</div> <div>Butanitol trinitrate</div> <div>Triethylene glycol dinitrate</div>

Cont.

**Table 4.2.4-12 (Cont.)
Typical Ingredients of Composite Solid Propellants**

Type	Percent	Acronym	Typical Chemicals
Energetic fuel binder	0-15	GAP	Glycidyl azide polymer
		PGN	Propyl glycidyl nitrate
		BAMO/AMMO	Bis-azidomethyloxetane/Azidomethyl-methyloxetane copolymer
		BAMO/NMMO	Bis-azidomethyloxetane/Nitramethyl-methyloxetane copolymer
Bonding agent	>0.5	MT-4	MAPO-tartaric acid-adipic acid condensate
		C1-diol	N-(2,2-dicyanoethyl)-2,3-dihydroxypropylene
		T-100/VCN/TEPANOL	Tetraethylenepentamine
		TEPAN	
		BP17	Bisphenol- α -glycidyl ether bonding agent
		BHEGA	N,N-bis(1-hydroxyethyl glycolimide)
Stabilizers	>0.5	DPA	Diphenyl amine
			Phenylnaphthyl amine
		NMA	N-methyl- <i>p</i> -nitroaniline
Processing aids	>0.5		Lecithin
			Sodium lauryl sulfate
			12-hydroxy stearate
		ADN	Adiponitrile
		Tween 21	Polyoxyethylene sorbitan monolaurate
		DC 200	Polydimethyl siloxane oil
			Dodecyl benzene sulfonic acid
		GMRO	Glyceryl monoricinoleate

Table 4.2.4-13 Classification of Solid Rocket Propellants Used in Flying Vehicles According to their Binders, Plasticizers, and Solid Ingredients

Designation	Binder	Plasticizer	Solid Oxidizer and/or Fuel	Propellant Application
Double base DB	Plasticized NC	NG, TA etc	None	Minimum signature and smoke
CMDDB ^a	Plasticized NC	NG, TMETN, TA, BTTN, etc	Al, AP, KP	Booster, Sustainer, and Spacecraft
	Same	Same	HMX, RDX, AP	Reduced smoke
	Same	Same	HMX, RDX, AZIDES	Minimum signature, gas generator
EMCDB ^a	Plasticized NC + elastomeric polymer	Same	Like CMDDB above, but generally superior mechanical properties with elastomer added to binder	
NEPE ^a	Plasticized NC	PEG	Al, AP	High energy strategic
Polybutadiene	HTPB	DOA, IDP, DOP, DOA, etc.	Al, AP, KP, HMX, RDX	Booster, Sustainer, or spacecraft, used extensively in many applications
	HTPB	Same	AN, HMX, RDX, some AP	Reduce smoke, gas generator
	CTPB, PBAN, PBAA	All like HTPB above, but lower performance due to lower solids content. Still used in applications with older designs.		
TPE ^{a,b}	Thermoplastic elastomer	Similar to HTPB, but without chemical curing process. TPEs cure (cross-link) via selective crystallization of certain parts of binder. Still experimental propellants.		
Polyether and polyesters	PEG, PPG, PCP, PGA and mixtures	DOA, IDP, TMETN, DEGDN, etc.	Al, AP, KP, HMX	Booster, Sustainer, or Spacecraft
Energetic binder (Other than NC)	GAP ^b , PGN, BAMO/NMMO, BAMO/AMMO	TMETN, BTTN, etc. GAP-azide GAP-nitrate	Like polyether/polyester propellants above but slightly higher performance. Experimental propellant	

^aCMDB composite modified double base; EMCDB elastomer modified cast double base; TPE Thermoplastic elastomer; NEPE nitrate ester polyether

^b TPE and GAP family of polymers are not currently used in any flying vehicle. For definitions of acronyms and abbreviations of propellant ingredients see Tables 4.2.4-11 and 4.2.4-12.

Two dimensional conventional structural formulae showing the repeating units for the energetic binders BAMO polymer and BAMO/AMMO copolymer are shown in Figure 4.2.4.2-1.

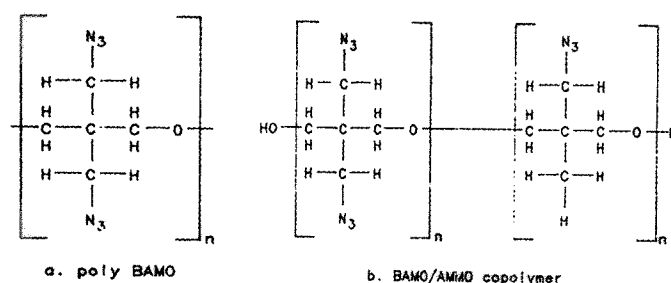


Figure 4.2.4.2-1 BAMO and BAMO/AMMO polymer structures.

Table 4.2.4-14 Exhaust Emissions from Typical Liquid, Hybrid, Solid Rocket Motors (Reference 4-18)
(LBm/SEC PER 100,000 LB THRUST)*

Species	L02/RP-1	Hybrid	Solid
Al ₂ O ₃	--	--	100.0
HCl	--	--	69.9
CO	134.8	137.0	79.8
CO ₂	93.6	103.9	11.7
H ₂ O	81.1	64.1	31.3
N ₂	--	1.2	29.0
H ₂	4.5	3.0	6.9
H	0.1	0.0	0.1
OH	0.0	0.1	0.1

*Theoretical calculations

4.2.4.3 Outdated/Historic Technology

- Conventional Liquid
LO₂-NH₃
- Hypergolic Liquid
HNO₃ - Furfuryl alcohol
- Conventional Solid
Polysulfide, solid oxidizer

4.2.4.4 Exhaust Species Quantization

The quantities of expected exhaust species from individual launches of various currently used vehicles are presented in Table 4.2.4-15, and projected annual releases for the year 2000 from solid propellant thrusters are listed in Table 4.2.4-16. These tables from Refs. 4-19 and 4-20 have been modified by inclusion of data for major US strategic vehicles. The data are for the fully expanded plumes at local ambient pressure, but do not include afterburning with atmospheric gases mixing, nor

chemical interactions due to cooling to ambient temperature. Thus, at low altitudes, almost all heated plume CO and H₂ would be oxidized to CO₂ and H₂O; at any altitude a significant level of NO_x will be formed from plume high temperature N₂ reaction with atmospheric O₂; as the plume cools HCl will react with plume or atmospheric H₂O vapor to form HCl.nH₂O vapor complexes that on further cooling will form droplets of hydrochloric acid.

Annual releases from liquid propellant thrusters are listed in Table 4.2.4-17. Table 4.2.4-18 shows the projected sums for all rocket for all launches. These tables were derived from Table 4.2.4-16 for this report. It is emphasized that the data in Tables 4.2.4-15 through 4.2.4-19 are based on expected or planned launches of vehicles using current technology for thrusters. They do not relate to advanced propellant compositions in Section 4.2.4.1 (Tables 4.2.4-1 to 4.2.4-4.) There is insufficient information at this time to project launches with advanced or environmentally benign propellants.

Table 4.2.4-15 Exhaust Quantities per Launch Vehicle (Reference 4-19)

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Atlas II (USA)	H ₂ O	21.5	18.0	20.5	70.0
	CO	32.2	19.1	5.1	56.4
	CO ₂	26.4	15.7	4.8	46.9
	H ₂	1.2	0.7	1.3	3.3

Cont.

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Atlas II, AS (USA)	H ₂ O				73.1
	CO				64.4
	CO ₂				47.9
	Al ₂ O ₃				10.0
	HCl				7.0
	H ₂				4.1
	N ₂				2.8
	OH				0.0
	H				0.0
STS(USA)	H ₂ O (SSME)	120.6	91.1	543.3	755.0
	H ₂ (SSME)	4.2	3.2	19.1	26.6
	H ₂ O (Total)	193.8	130.5		867.7
	Al ₂ O ₃ (Total)	234.0	126.0		360.0
	CO (Total)	186.7	101.0		287.3
	HCl (Total)	163.3	88.0		251.3
	N ₂ (Total)	67.9	36.5		104.4
	CO ₂ (Total)	27.4	14.7		42.1
	H ₂ (Total)	20.4	11.9		51.4
	FeCl ₂ (SRM)(Ref. 4-21)	1.8	4.3		6.1
	Cl(SRM)(Ref. 4-21)	0.9	2.1		3.0
	OH (Total)	0.2	0.1		0.4
	H (Total)	0.2	0.1		0.4
	Fe(SRM)(Ref. 4-21)	0.06	0.14		0.2
Delta II (USA)	CO (Liquid Motor)	10.2	10.3	24.2	44.7
	CO ₂ (Liquid Motor)	7.7	7.8	20.1	35.6
	H ₂ O (Liquid Motor)	6.2	6.3	15.7	28.1
	N ₂ (Liquid Motor)			2.2	2.4
	H ₂ (Liquid Motor)	0.4	0.4	1.0	1.7
	CO (Total)				62.6
	CO ₂ (Total)				38.3
	H ₂ O (Total)				35.2
	Al ₂ O ₃				22.5
	HCl (Total)				15.7
	N ₂ (Total)				8.9
	H ₂ (Total)				3.3
	OH (Total)				0.0
	H (Total)				0.0

Cont.

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Titan IV (USA)	N ₂ (Liquid Motor)		9.4	80.1	89.5
	H ₂ O (Liquid Motor)		7.5	62.7	70.2
	CO ₂ (Liquid Motor)		3.7	32.5	36.2
	CO (Liquid Motor)		1.1	9.3	10.4
	H ₂ (Liquid Motor)		0.1	1.3	1.5
	CO (Total)				142.1
	N ₂ (Total)				138.4
	H ₂ O (Total)				121.8
	HCl (Total)				115.3
	CO ₂ (Total)				55.0
	H ₂ (Total)				12.9
	Al ₂ O ₃				11.5
	OH (Total)				0.2
	H (Total)				0.2
Minuteman I-III, Stage I (USA)	Al ₂ O ₃	6.16			6.16
	CO	4.89			4.89
	HCl	4.39			4.39
	H ₂ O	1.94			1.94
	N ₂	1.79			1.79
	CO ₂	0.75			0.75
	H ₂	0.42			0.42
	Cl	0.03			0.03
	AlCl ₂	0.01			0.01
Minuteman III, Stage II (USA)	CO ₂		2.12		2.12
	Al ₂ O ₃		1.75		1.75
	HCl		1.09		1.09
	H ₂ O		0.50		0.50
	N ₂		0.44		0.44
	H ₂		0.13		0.13
	CO		0.10		0.10
	Cl		0.01		0.01
Minuteman III, Stage III (USA)	Al ₂ O ₃		0.94		0.94
	HCl		0.72		0.72
	CO		0.69		0.69
	H ₂ O		0.40		0.40
	N ₂		0.28		0.28
	CO ₂		0.15		0.15
	H ₂		0.06		0.06

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Peacekeeper, Stage I	Al ₂ O ₃	15.71			15.71
Ref. 4-22 (USA)	CO	9.69			9.69
	HCl	9.29			9.29
	N ₂	3.67			3.67
	H ₂ O	3.26			3.26
	H ₂	0.98			0.98
	CO ₂	0.94			0.94
	Cl	0.08			0.08
Peacekeeper, Stage II	Al ₂ O ₃		9.16		9.16
Ref. 4-22 (USA)	CO		5.71		5.71
	HCl		5.04		5.04
	N ₂		1.97		1.97
	H ₂ O		1.31		1.31
	H ₂		0.58		0.58
	CO ₂		0.40		0.40
	AlCl		0.01		0.01
Peacekeeper, Stage III	CO		2.42		2.42
Ref. 4-22 (USA)	Al ₂ O ₃		2.23		2.23
	N ₂		1.65		1.65
	H ₂ O		0.20		0.20
	CO ₂		0.19		0.19
	H ₂		0.16		0.16
	HCl		0.11		0.11
ASROC (USA)	CO	0.06			0.06
	CO ₂	0.02			0.02
	H ₂ O	0.01			0.01
	N ₂	0.01			0.01
Tartar (USA)	HCl	0.05			0.05
	CO	0.04			0.04
	CO ₂	0.04			0.04
	H ₂ O	0.04			0.04
	N ₂	0.03			0.03
	Al ₂ O ₃	0.03			0.03

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Terrier Booster (USA)	CO	0.20			0.20
	CO ₂	0.19			0.19
	N ₂	0.07			0.07
	H ₂ O	0.06			0.06
	H ₂	0.01			0.01
	Pb	0.01			0.01
Terrier Sustainer (USA)	HCl	0.05			0.05
	CO ₂	0.04			0.04
	H ₂ O	0.04			0.04
	N ₂	0.02			0.02
	CO	0.01			0.01
Titan II (USA)	N ₂	9.9	23.1	27.6	60.7
	H ₂ O	7.8	18.1	21.5	47.5
	CO ₂	4.0	9.4	11.2	24.6
	CO	1.2	2.7	3.2	7.0
	H ₂	0.2	0.4	0.4	1.0
RSLP					
Minuteman I&II, Stage I (USA)	Al ₂ O ₃	6.16			6.16
	CO	4.89			4.89
	HCl	4.39			4.39
	H ₂ O	1.94			1.94
	N ₂	1.79			1.79
	CO ₂	0.75			0.75
	H ₂	0.42			0.42
	Cl	0.03			0.03
	AlCl ₂	0.01			0.01
Minuteman I, Stage II (USA)	Al ₂ O ₃		1.29		1.29
	HCl		1.11		1.11
	CO		0.97		0.97
	H ₂ O		0.57		0.57
	N ₂		0.40		0.40
	CO ₂		0.21		0.21
	H ₂		0.09		0.09
	Cl		0.01		0.01

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Minuteman I, Stage III (USA)	CO		0.80		0.80
	N ₂		0.27		0.27
	H ₂ O		0.16		0.16
	HCl		0.15		0.15
	Al ₂ O ₃		0.10		0.10
	CO ₂		0.10		0.10
	H ₂		0.04		0.04
	Cl		0.01		0.01
Minuteman II, Stage II (USA)	CO ₂		1.60		1.60
	Al ₂ O ₃		1.32		1.32
	HCl		0.82		0.82
	H ₂ O		0.38		0.38
	N ₂		0.33		0.33
	CO		0.08		0.08
	H ₂		0.10		0.10
	Cl		0.01		0.01
Minuteman II, Stage III (USA)	CO		0.80		0.80
	N ₂		0.27		0.27
	H ₂ O		0.16		0.16
	HCl		0.15		0.15
	Al ₂ O ₃		0.10		0.10
	CO ₂		0.10		0.10
	H ₂		0.04		0.04
	Cl		0.01		0.01
Talos (USA)	CO ₂	0.46			0.46
	CO	0.45			0.45
	N ₂	0.17			0.17
	H ₂ O	0.13			0.13
	H ₂	0.02			0.02
	Pb	0.02			0.02
Sergeant (USA)	CO ₂	0.68			0.68
	CO	0.40			0.40
	HCl	0.53			0.53
	H ₂ O	0.49			0.49
	H ₂ S	0.29			0.29
	N ₂	0.22			0.22
	H ₂	0.03			0.03

Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
ORBUS (USA)	CO				
	CO ₂				
	H ₂				
	H ₂ O				
	N ₂				
	HCl				
	OH				
	H				
Ariane 5 (Europe)	Al ₂ O ₃				
	H ₂ O (Liquid Motor)				56.7
	N ₂ (Liquid Motor)				14.9
	CO ₂ (Liquid Motor)				6.0
	H ₂ (Liquid Motor)				1.8
	CO (Liquid Motor)				1.7
	Al ₂ O ₃				132.1
	CO (Total)				115.9
	H ₂ O (Total)				101.4
	HCl (Total)				60.0
	N ₂ (Total)				51.4
	CO ₂ (Total)				22.8
	H ₂ (Total)				11.7
	OH (Total)				0.1
	H (Total)				0.1
Energia (CIS)	H ₂ O				1,317.6
	CO				621.5
	CO ₂				431.5
	H ₂				54.0
	H				0.5
Zenit (CIS)	CO				783.1
	CO ₂				543.7
	H ₂ O				473.0
	H ₂				26.1
	H				0.6

**Table 4.2.4-15 (Cont.)
Exhaust Quantities per Launch Vehicle**

Launch Vehicle	Exhaust Product	Mass Per Flight (tons)			Total Mass (tons)
		0-15 km	16-50 km	>50 km	
Long March (China)	N ₂				115.5
	CO ₂				41.7
	H ₂ O				40.6
	CO				13.4
	H ₂				1.8
H-2 (Japan)	H ₂ O (Liquid Motor)				82.3
	H ₂ (Liquid Motor)				2.9
	H ₂ O (Total)				103.2
	Al ₂ O ₃ (Total)				61.9
	CO (Total)				53.4
	HCl (Total)				46.7
	CO ₂ (Total)				7.8
	H ₂ (Total)				7.5
	N ₂ (Total)				1.9
	OH (Total)				0.1
	H (Total)				0.1

**Table 4.2.4-16 Annual Exhaust Quantities for Solid Propulsion Motors of all Launch Vehicles
Projected for Year 2000 (Reference 4-20)**

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR
Atlas II-AS (based on 8 launches per year)	CO	515
	CO ₂	383
	H ₂	33
	H ₂ O	585
	N ₂	22
	HCl	56
	OH	0.1
	H	0.1
	Al ₂ O ₃	80

Table 4.2.4-16 (Continued)
Solid Propulsion Motors
of all Launch Vehicles Projected for Year 2000

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR
Delta II (based on 8 launches per year)	CO	144
	CO ₂	21
	H ₂	12
	H ₂ O	56
	N ₂	52
	HCl	126
	OH	0.2
	H	0.2
	Al ₂ O ₃	180.
STS (based on 10 launches per year)	CO	2,873
	CO ₂	421
	H ₂	248
	H ₂ O	1,127
	N ₂	1,044
	HCl	2,513
	OH	3.6
	H	3.6
	Al ₂ O ₃	3,600
Titan IV (based on 10 launches per year)	CO	1,317
	CO ₂	193
	H ₂	115
	H ₂ O	516
	N ₂	489
	HCl	1,153
	OH	1.7
	H	1.7
	Al ₂ O ₃	1,650
Minuteman III (based on 3 launches per year)	CO	17.04
	CO ₂	9.06
	H ₂	1.83
	H ₂ O	8.52
	N ₂	7.53
	HCl	18.6
	Al ₂ O ₃	26.55
	AlCl ₃	0.03
	Cl	0.12

Cont.

Table 4.2.4-16 (Continued)
Solid Propulsion Motors
of all Launch Vehicles Projected for Year 2000

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR
Peacekeeper (based on 3 launches per year)	CO	53.46
	CO ₂	4.59
	H ₂	5.16
	H ₂ O	14.31
	N ₂	21.87
	HCl	43.32
	Al ₂ O ₃	81.3
	AlCl ₂	0.03
	Cl	0.24
RSLP (based on 26 launches per year, half Minuteman II Stage II, half Stage III half TALOS, half Sergeant)	CO	22.49
	CO ₂	36.92
	H ₂	2.47
	H ₂ O	15.08
	N ₂	12.87
	HCl	19.5
	Al ₂ O ₃	18.46
	Cl	0.26
	Pb	0.26
	H ₂ S	3.77
Ariane 5 (based on 9 launches per year)	CO	1,027
	CO ₂	151
	H ₂	89
	H ₂ O	403
	N ₂	373
	HCl	900
	OH	1.3
	H	1.3
	Al ₂ O ₃	1,287

Cont.

Table 4.2.4-16 (Continued)
Solid Propulsion Motors
of all Launch Vehicles Projected for Year 2000

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR
H-2 (based on 2 launches per year)	CO	107
	CO ₂	16
	H ₂	9
	H ₂ O	42
	N ₂	39
	HCl	93
	OH	0.1
	H	0.1
	Al ₂ O ₃	134
TOTALS	CO	6,075
	CO ₂	1,236
	H ₂	513
	H ₂ O	2,767
	N ₂	2,062
	HCl	4,562
	OH	7.0
	H	7.0
	Al ₂ O ₃	7,057
	AlCl ₃	0.06
	Cl	0.63
	Pb	0.28
	H ₂ S	3.77
<hr/>		
Solid Motors:	Sum	24,290 = 54 M pounds

**Table 4.2.4-17 Annual Exhaust Quantities for Liquid Propulsion Engines of all Launch Vehicles
Projected for Year 2000**

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR
Atlas II (USA) (based on 8 launches per year)	CO	451
	CO ₂	375
	H ₂	26
	H ₂ O	560
STS(SSME) (USA) (based on 10 launches per year)	H ₂	266
	H ₂ O	7550
Delta II (USA) (based on 8 launches per year)	CO	358
	CO ₂	285
	H ₂	14
	H ₂ O	225
Titan II (USA) (based on 5 launches per year)	N ₂	19
	CO	35
	CO ₂	123
	H ₂	5
Titan IV (USA) (based on 10 launches per year)	H ₂ O	238
	N ₂	304
	CO	104
	CO ₂	362
Ariane 5 (Europe) (based on 9 launches per year)	H ₂	15
	H ₂ O	702
	N ₂	895
	CO	15
	CO ₂	54
	H ₂	16
	H ₂ O	510
	N ₂	134

Cont.

Table 4.2.4-17 (Cont.)
Annual Exhaust Quantities for
Liquid Propulsion Engines
of all Launch Vehicles Projected for Year 2000

LAUNCH VEHICLE	EXHAUST PRODUCT	TONS/YR	
Energia (CIS) (based on 8 launches per year)	CO	4,972	
	CO ₂	3,452	
	H ₂	432	
	H ₂ O	10,541	
	H	4	
Zenit (CIS) (based on 6 launches per year)	CO	4,700	
	CO ₂	3,262	
	H ₂	157	
	H ₂ O	2,838	
	H	4	
Long March (China) (based on 2 launches per year)	CO	27	
	CO ₂	83	
	H ₂	4	
	H ₂ O	81	
	N ₂	231	
H-2 (Japan) (based on 2 launches per year)	H ₂	6	
	H ₂ O	165	
TOTALS	CO	10,662	
	CO ₂	7,996	
	H ₂	941	
	H ₂ O	22,710	
	N ₂	1,583	
	H	8	
<hr/>			
Liquid Engines:	Sum	43,900	= 98 M pounds

**Table 4.2.4-18 Annual Exhaust Quantities for All Launch Vehicles
Projected for Year 2000**

EXHAUST PRODUCT	TONS/YR	
CO	16,737	
CO ₂	9,232	
H ₂	1,454	
H ₂ O	25,477	
N ₂	3,645	
HCl	4,562	
OH	7.0	
H	15.0	
Al ₂ O ₃	7,057	
AlCl ₃	0.06	
Cl	0.63	
Pb	0.28	
H ₂ S	3.77	
<hr/>		
All Vehicles:	Sum	68,190 = 152 M pounds

A presentation at a NASA-sponsored conference on environmentally suspect aerospace materials, Ref. 4-23, reported that in the USA, 15 Mlb of waste are generated from propulsion development and manufacturing, as summarized in Figure 4.2.4.4-1 following, copied from the reference. In the figure, about 40% of the 15 Mlb, or 6 Mlb, is exhaust from firing tests; this number does not include vehicle application launches.

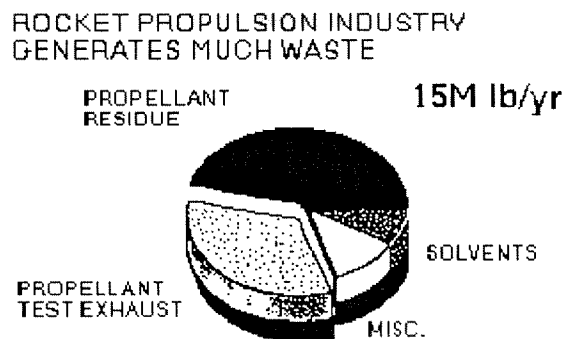


Figure 4.2.4.4-1. Rocket Industry Waste Source Distribution

The US launches tabulated above have total exhausts summing to 73 Mlb; the additional 6 Mlb from testing, if assumed still applicable in the year 2000, raises the total exhaust generated to 79 Mlb. If the same ratio of test to application applies to other nations, then the world total production of rocket exhausts will be 164 Mlb. On the assumption that the annual averaged test exhaust composition is the same as those from vehicle launches, the increased total weights for constituents were calculated by ratioing; they are shown in Table 4.2.4-19.

Table 4.2.4-19 Annual Exhaust Quantities for All Launch and Test Firings Projected for Year 2000

EXHAUST PRODUCT		TONS/YR
CO	18,058	
CO ₂	9,960	
H ₂	1,468	
H ₂ O	27,488	
N ₂	3,933	
HCl	4,922	
OH	8.0	
H	16.0	
Al ₂ O ₃	7,614	
AlCl ₃	0.06	
Cl	0.68	
Pb	0.30	
H ₂ S	4.85	

World Wide Launch plus U.S. Test Exhaust:	Sum	73,472 = 164 M pounds

4.2.4.5 Altitude Differentiation

4.2.4.5.1 Ground Cloud and Plume Shape

The ground cloud has been defined as "That cloud of rocket effluents emitted during the initial phase of vehicle launch. This cloud is assumed to have an ellipsoidal shape.", Ref. 4-24. Another definition, by the same author, is "the portion of the plume that is trapped in the (local atmospheric) surface transport layer.", in the REED model, Ref. 4-25.

Formation of rocket ground cloud involves impingement of the plume on the launching structure, a flame deflector and a trench or flow of cooling water. The cloud forms from high temperature exhaust gases ($>2000\text{ K}$) and vaporized cooling water. The hot cloud rises, radiating energy while incorporating and reacting with ambient air. For an "instantaneous source" vehicle, typically a solid propellant rocket such as Titan III, the inflow of entrained air is spherically symmetrical. The altitude reached by the rising cloud is that at which buoyant equilibrium with the ambient atmosphere is attained, typically 1-2 km, in about 10 minutes, and starts to drift with local winds. For a "continuous source" such as the STS, the cloud is cylindrical and initially extends to the 1-2 km height, and entrainment is cylindrical, at the sides only (Ref. 4-26).

At stabilization, the cloud typically consists of 99.9 percent entrained air, and virtually all hydrogen and CO have afterburned to water and CO_2 (Ref. 4-25.) Formation of nitrogen oxides from elemental O_2 and N_2 occurs in any region containing the gases while the region temperature is above $2000\text{ }^\circ\text{K}$. Alumina particles, Al_2O_3 , can absorb water and hydrogen chloride, HCl , from the vapor phase of the plume, dissolving a surface layer of the Al_2O_3 and forming a strongly acidic solution of aluminum chloride hexahydrate, Ref. 4-27.

A diagram of the instantaneous source process, copied from Ref. 4-25 is shown in Figure 4.2.4.5-1.

An evaluation of this model (abbreviated as MDM, not REED) and several others - Meteorological Effluent Transport, (METS), Reference 4-28; TREATS model, Reference 4-29; Atmospheric Diffusion, Particle-in-Cell (ADPIC) Model; Reference 4-30; Diffusion in Shear Flow (DISF), Reference 4-31) - using meteorological measurements on the ground and by aircraft subsequent to Titan launches (Reference 4-32), and also presents the Cloud Rise Aerosol Model (CRAM) to overcome calculate interactions between different aerosols in a ground cloud. A summary of the conclusions includes:

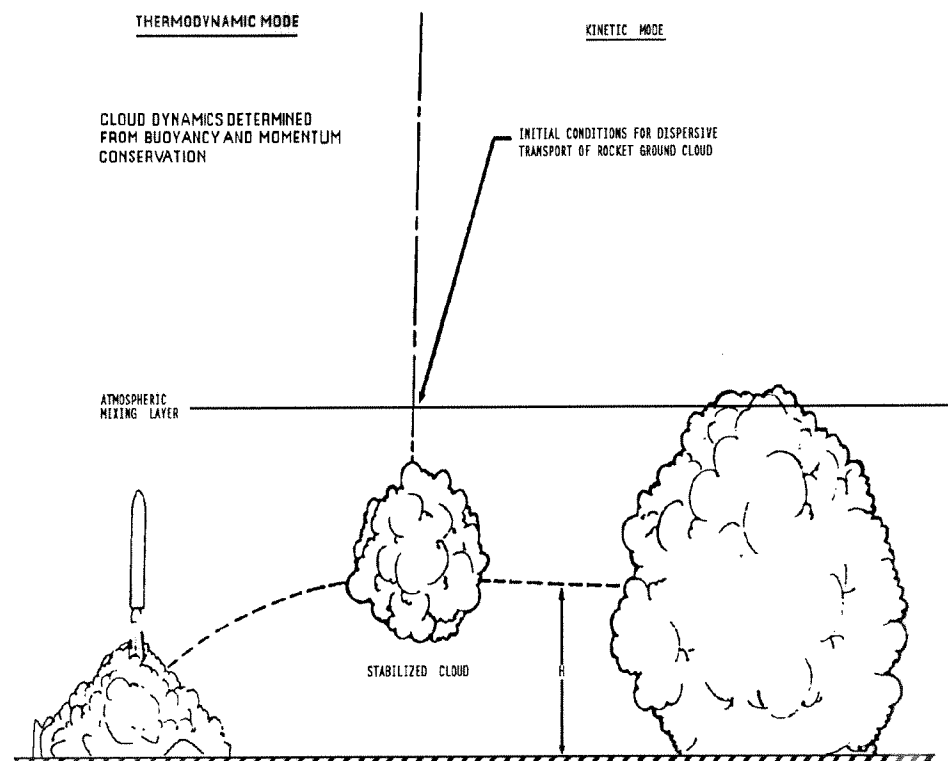


Figure 4.2.4.5-1. Ground Cloud Formation and Transport

(1) MDM consistently over predicts maximum ground level concentrations when the input standard deviation of the azimuth angle is chosen appropriately. This actually accepted as a positive feature because it supplies 'conservative' values for evaluating environmental hazards.

(2) The high values at ground level may be due to assumptions of strong turbulence in the upper portion of the cloud, and result in under predicted concentrations above ground level.

(3) When the atmospheric mixing layer is shallow, atmospheric entrainment is overestimated, resulting in too low calculated pollutant concentrations.

(4) The uncertainty about the mass and size distribution of debris swept from the ground is too great.

(5) The more exactly formulated models, TREATS, ADPIC, and DISF, demonstrate approaches to improve diffusion modeling in MDM.

(6) Improve heat flux measurements near ground height are needed.

(7) Collection of improved aerosol characterization launch test data is needed; size distribution and chemical composition.

Figure 4.2.4.5-2, after Figure 18-1 in Reference 4-16, shows the typical structure of a plume at heights up to 18 km. In the near field there is an inviscid core of exhaust gases that have not yet

mixed with ambient air and a relatively thin outer layer where oxygen from the air burns turbulently with the combustible portions of the exhaust from a typically fuel-rich thruster. Species such as H_2 , CO , NO , or CH_2 are largely burned to H_2O , CO_2 , or NO_2 , and the heat of this secondary combustion raises the temperature and volume of the afterburning layer. In the intermediate field the shock wave intensities decrease and more of the mass flow is mixed with the air. In the far field the exhaust and ambient air are well mixed throughout a cross section of the plume and local plume pressure is essentially ambient. The core of the plume emerges supersonically from the nozzle, goes through an oblique compression shock wave, called the barrel wave. The central part of the plume forms the Mach disk, a strong normal compression wave; the gases slow and increase in pressure and temperature. The flow is subsonic for a short distance, then becomes supersonic again. A pattern of repeated Mach disks and short subsonic regions becoming supersonic is repeated several times in the core of the plume, forming the Mach diamond phenomenon. This description is somewhat different from the REED model.

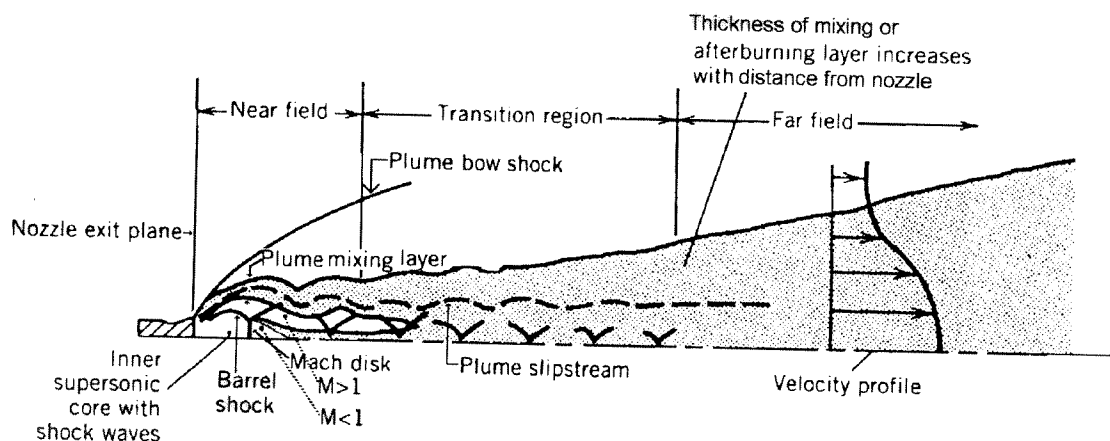
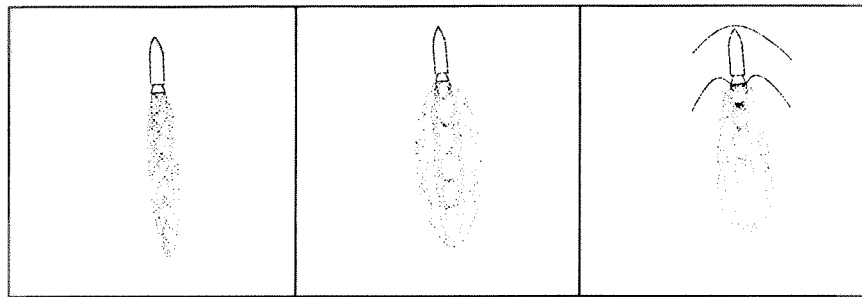


Figure 4.2.4.5-2 Half-section schematic of low altitude plume

The size, shape, and internal structure of a plume changes dramatically with altitude. Figure 4.2.4.5-3, after Figure 18-2 in Reference 4-16, shows sketches of the variation of the plume configuration with altitude. When the nozzle exit pressure is approximately equal to the ambient pressure (condition for optimum nozzle expansion), the plume has a long, nearly cylindrical shape. With increasing altitude the plume shape becomes more of a cone and the plume length and diameter increase.



Inner supersonic core	Narrow, several shock diamonds	Larger diameter, some shockwave pattern,	Only one or two sets of shock waves are visible fewer visible shock waves
Mixing layer Nozzle exit pressure P_2 and ambient pressure P_3	Narrow $P_2 \equiv P_3$	Wider, unsteady, turbulent $P_2 > P_3$	Very wide, irregular (afterburning) $P_2 \gg P_3$
Flight velocity	Very low, subsonic	Subsonic, transonic and slightly supersonic	Supersonic
Altitude, km	0 to 5	10 to 25	Above 35

Figure 4.2.4.5-3 Plume Growth in Length and Diameter as the Rocket Gains Altitude

The afterburning of the fuel-rich combustion products with oxygen from the air occurs in the mixing layer. At very high altitudes above 200 km there is no air and therefore no afterburning.

4.2.4.5.2 Plume Cloud

The Plume Cloud has been defined as “The cloud of rocket effluents emitted from the vehicle in flight. This cloud has a cylindrical shape...”, Refs. 4-24 and 4-33. Additional wording in the reference implies that the generation of the plume cloud is considered to start from combustion at or above the “atmospheric mixing layer” shown in Figure 4.2.4-1; it is not confined to upper stage operation.

Calculated concentrations of various combustion products laterally along the exhaust plume centerline from LOX/RP-1 that are plotted as a function of axial distance demonstrate the effects of afterburning in Figure 4.2.4.5-4.

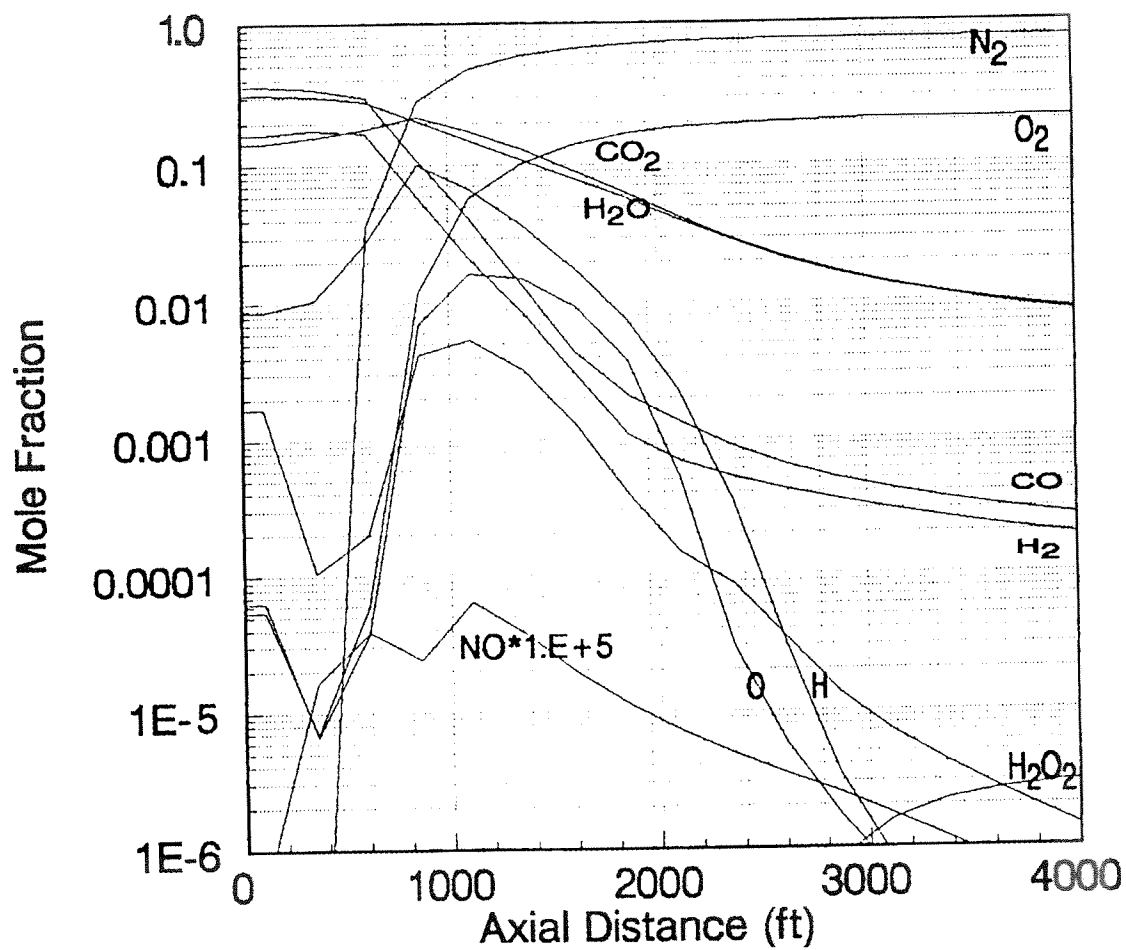


Figure 4.2.4.5-4 Effect of Afterburning on Composition of LOX/RP-1 Plume.

4.2.4.5.3 Propellant Systems Effects

Concentrations of significant species in exhaust Ground and Plume Clouds from Advanced Propellants are listed below, in Table 4.2.4-20, in which the exhaust species concentrations are abstracted from Tables 4.2.4-1 to 4.2.4-4. The chemical effects of afterburning with entrained atmospheric species are reported.

Table 4.2.4-20 Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Gas; Monopropellant		
H ₂	H ₂ ; H ₂ O;	2240 --
NH ₃	NH ₃ ; H ₂ ; N ₂ ; NO _x ; H ₂ O;	2240 -- -- -- --
Xe	Xe;	2240
Li	Li; Li ₂ O;	2240 --
Gas; Bipropellant		
H ₂ +O ₂	H ₂ O;	2164
ACS:	H ₂ ;	76
MD/X	NO _x ;	
Liquid; Monopropellant; Gelled		
Alumizine (Al-gelled hydrazine)	H ₂ ; N ₂ ; NH ₃ ; AlN; H ₂ O; Al ₂ O ₃ NO _x ;	
Liquid; Bipropellant; Hypergolic		
LH ₂ +LF ₂	HF; H ₂ ; H; F; H ₂ O;	1761 6.7 2.2 470

Table 4.2.4-20 (Cont.)
Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Liquid; Bipropellant; Hypergolic (Cont.)		
N ₂ H ₄ + N ₂ F ₄	HF;	1290
	N ₂ ; H ₂ O; NO _x ;	950
N ₂ H ₄ + ClF ₅	HF;	1228
	HCl;	470
	N ₂ ;	542
	H ₂ O; NO _x ;	
B ₂ H ₆ + OF ₂	HF;	694
	H ₂ O;	329
	B ₂ O ₃	426
	BF ₃ ;	797
	NO _x ;	
C ₂ H ₄ + OF ₂	HF;	1519
	H ₂ O;	47
	CO;	123
	CO ₂ ;	132
	CF ₄ ;	421
	NO _x ;	
Liquid; Bipropellant; Gelled; Hypergolic		
F ₂ (gel) + N ₂ H ₄ (gel)	HF;	1635
	N ₂ ;	603
	PF ₅ ;	0.6
	CO;	0.6
	CF ₄ ;	0.4
	NO _x ;	
Gel F ₂ + Gel H ₂	HF;	1758
	H ₂ ;	6.7
	H;	2.2
	F;	450
	CF ₄ ;	0.7
	CO;	0.4
	PF ₅ ;	0.7

Table 4.2.4-20 (Cont.)
Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Liquid; Bipropellant; Gelled; Hypergolic (Cont.)		
Gel F ₂ + Gel NH ₃	HF;	1796
	N ₂ ;	441
	CF ₄ ;	0.4
	CO;	0.7
	PF ₅ ;	0.7
	NO _x ;	
N ₂ H ₄ + IRFNA (with gelling solids)	H ₂ ;	
	H ₂ O;	
	Li ₂ O;	
	CO;	
	CO ₂ ;	
	SiO ₂ ;	
	N ₂ ; NO _x ;	
N ₂ H ₄ + IRFNA (with low smoke gelling solids)	H ₂ ;	
	H ₂ O;	
	CO;	
	CO ₂ ;	
	N ₂ ; NO _x ;	
Liquid-Slush		
H ₂ (slush) + LO ₂	H ₂ ;	76
	H ₂ O;	2164
	NO _x ;	
Liquid-Solid Hybrid		
LO ₂ + Butyl rubber	H ₂ ;	22
	H ₂ O;	452
	CO;	997
	CO ₂ ;	753
	OH;	1
	N;	9
	NO _x ;	
Liquid-Solid Hybrid; Hypergolic		
LiBH ₄ + H ₂ O ₂	H ₂ ;	
	H ₂ O;	1720
	Li ₂ O;	132
	B ₂ O ₃	385

Table 4.2.4-20 (Cont.)
Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Liquid; Tripropellant		
LO ₂ +	H ₂ ;	2
[LH ₂ +	H ₂ O;	1814
CH ₄ / RP-	CO;	101
1]	CO ₂ ;	314
	Li ₂ O;	
	B ₂ O ₃	
	NO _x ;	
Solid; H, C, O, Cl Free		
NF ₄ BF ₄ +	PF ₅ ;	1389
Li + Poly	BF ₃ ;	249
PNF ₂	N ₂ ;	258
	LiBF ₄	345
	NO _x ;	
	PN;	
	BN;	
	P ₂ O ₅	
	B ₂ O ₃ ;	
Solid; Cl-free exhaust		
GAP +	H ₂ ;	
TMETN +	H ₂ O;	
AN	CO;	
	CO ₂ ;	
	N ₂ ;	
	NO _x ;	
Solid; HCl-free exhaust		
PGA +	CO;	
TEGDN +	CO ₂ ;	
ZnO-Stab-	H ₂ ;	
ilized AN	H ₂ O;	
+ MgAl	N ₂ ;	
	NO _x ;	
	MgO;	
	ZnO;	
	Al ₂ O ₃	
HTPE +	CO;	
BuNENA	CO ₂ ;	
+ Amine	H ₂ ;	
phase-	H ₂ O;	
stabilized	N ₂ ;	
AN +	NO _x ;	
MgAl	MgO;	
	Al ₂ O ₃	

Table 4.2.4-20 (Cont.)
Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Solid; HCl-free exhaust (Cont.)		
HAN/AN + Al + PVA	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃	
Solid; Neutralized HCl		
HTPE + AN + AN + MgAl	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; MgO; Al ₂ O ₃ MgCl ₂	
Solid; Scavenged HCl		
HTPB + DOA + Al + NaNO ₃ + AP + 0.8% KP	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ NaCl; KCl; Na ₂ O; K ₂ O; NaOH; KOH;	

Table 4.2.4-20 (Cont.)
Exhaust Constituents from Advanced Propellants

Nominal Exhaust Composition, lb/ton propellant		
Solid; Scavenged HCl (Cont.)		
HTPB + AP + NaNO ₃ + HMX + Al	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ NaCl; Na ₂ O; NaOH;	
Solid; Decreased HCl		
AP, Al, CTPB, BITA, Polybutene HAN, PVA	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ HCl;	45

4.2.5 Assessment Approach; Criteria/Standards; Ratings

Assessment of environmental effects of operation of rocket propelled vehicles faces several distinct issues: 1). the criteria for deleterious environmental effects A). currently do not include many of the species released by propellant combustion known or suspected to be deleterious to some aspects of the environment; B). do not address release of chemicals at altitudes significantly above ground level; or C). some criteria evaluation approaches are inappropriate for transient exhaust emission (e.g., acid rain criteria); and 2). the criteria for evaluating rocket system performance are typically specific for individual systems and do not provide adequate figures of merit for intersystem comparison.

4.2.5.1 Environmental

sources: EPA, Montreal Protocol,
 Propellant Waste Management, Ref. 4-34
 National Environmental Protection Act (NEPA), Ref. 4-35
 Clean Air Act as Ammended (CAAA) Ref. 4-36

Undesirable effects of chemical species on the environment are generally called Pollution, and this may apply to contamination of the atmosphere, Air Pollution, oceans, fresh, and ground water, and the ground. Operationally, these are not exclusive; for instance Air Pollution with chemically stable and soluble species can lead to water and ground pollution through Acid Rain and settling.

In the current project, the emphasis is on production of air-borne pollutants by the combustion of rocket propellants during vehicle launch activities. Environmental effects occurring during manufacture of the rocket propellant and rocket systems hardware are specifically excluded.

President Clinton's Executive Order 12856, Ref. 4-2, requires pollution prevention to the toxic levels of chemical substances specified in Section 313(e) of EPCRA (The Emergency Planning and Community Right-To-Know Act) Ref. 4-3. The Presidential "Climate Change Action Plan", Ref. 4-1, requires reduction of use and emissions of CH₄, nitrous oxide, and the CFC (Chlorofluorocarbon) substitutes HFC-23, CF₄, and C₂F₆. The Pollution Prevention Act of 1990, Ref. 4-4, states that pollution should be prevented or reduced at its source, and that release into the atmosphere is to be conducted in an "environmentally safe manner."

The division of plume constituent effects into several environmental and safety categories as followed in this document is highly artificial and reflects the charters of the various regulatory agencies. For instance, HCl is toxic, is a constituent of acid rain, is a potential stratospheric ozone depletion intermediate, etc. The regulated or suggested concentration limits for these interactions are all different. Additionally, the geographic locations where they occur are also different. Low altitude effects, toxicity and acid rain, can require different, and usually higher, maximum limits than high altitude effects at very low concentration, e.g., ozone reactivity, unless it is shown that low altitude releases can be naturally transported to high altitude, which then imposes the more stringent limits at low altitude.

The rocket propulsion industry has developed a terminology to classify exhaust "properties" (sic., compositions). Although some of these are of interest from environmental considerations, classifications based on this terminology should be avoided as there are no hard-and-fast quantitative definitions, so use of the terms themselves and their application to specific propellants are pretty much up to an individual author's objectives.

The following summarizes the definitions, condensed from the listing in Ref. 4-37.

SMOKY- Propellants whose exhaust products contain particulate matter such as Al₂O₃, which appears in the exhaust stream as smoke, called *primary* smoke.

CLEAN- 'Smoky' propellants formulated to reduce HCl emission to less than 1 % of the exhaust *gas*.

REDUCED SMOKE- Propellants without metals or primary smoke, but which produce HCl as a primary combustion product: if the HCl is injected into an atmosphere of high or moderate humidity, water droplets will coalesce on the HCl molecules resulting in a visible trail called secondary smoke ; in atmospheres of low humidity, no visible trail is produced. [Author's comment: note that effects of high altitude contrails from water in the exhaust itself interacting with HCl vapor is ignored.]

MINIMUM SMOKE- Propellants with no metals and exhaust free of nucleating species such as HCl. (Appears to be synonym for 'clean reduced smoke'.)

MINIMUM SIGNATURE- 'Minimum smoke' with low visible, infrared and ultraviolet emission.

SCAVENGER- A propellant containing sufficient alkali metal (such as sodium compounds) to react with all HCl released and form NaCl. This particular characteristic seems

to be valued for reduction of plume toxicity, and is not correlated with plume detectability as are the other characteristics.

Numerical methods to define a candidate alphabetical rating scale for smoke characteristics of solid propellant exhausts (Ref. 4-38) have been developed and proposed by the NATO Advisory Group for Aerospace Research and Development, AGARD, (Ref. 4-39). It is pointed out that the approach is not completely applicable to fully integrated rocket motors because components such as ignitors, liners, insulators, nozzle materials, etc., must also be considered as smoke sources.

Smoke characteristics are defined by a pair of letters, each of which has the range of A to C, where A indicates minimum smoke and C indicates maximum smoke. The first letter of the pair refers to 'primary' smoke, i.e., condensed materials in the exhaust plume. The second letter refers to 'secondary' smoke from the condensation of water vapor or water vapor and the acids HF and HCl. A chart indicating the grades is shown:

	Increasing Secondary Smoke →		
Increasing 	AA	AB	AC
Primary ↓	BA	BB	BC
Smoke	CA	CB	CC

An AA propellant could be considered a minimum smoke propellant; AC, a reduced smoke propellant; and CC, a smoky propellant on the rocket industry scale.

The Primary scale, AGARDP, is calculated by the following steps:

1. Determine the exhaust composition by using an adiabatic combustion code at a chamber pressure of 70 atm and an exit pressure of 1 atm. Record the mass percentages of each condensable product at shifting equilibrium.

2. Calculate the AGARDP number = $1 - \exp[-\sum_i \{\%M_{pi} N_i / SG_i\}]$

where $\%M_{pi}$, SG_i , and N_i are the mass percentage, specific gravity, and optical property constant (currently taken as 1) of each of the condensable species i .

3. Assign the ASGARDP Class as follows:

ASGARDP number	ASGARDP Class
$ASGARDP \leq 0.35$	A
$0.35 < ASGARDP \leq 0.9$	B
$ASGARDP > 0.9$	C

A quick procedure for calculating the secondary scale, AGARDS, is outlined in the following steps:

1. Determine the mole fraction concentrations in the exhaust plume of water vapor (H_2O), HF, and HCl at shifting equilibrium. Divide the acid vapor concentrations by 1000.
2. From Figure 4.2.5.1-1, select the curve which best represents the halogen acid vapor exhaust fraction and select a point on the curve whose abscissa represents the water vapor mole fraction. The ordinate of the selected point is the relative humidity required for saturation (secondary smoke formation). When extended to the right hand scale, the ordinate defines the AGARDS secondary smoke classification, A, B, or C.
3. Combine the AGARDP and AGARDS Class letters for the overall classification.

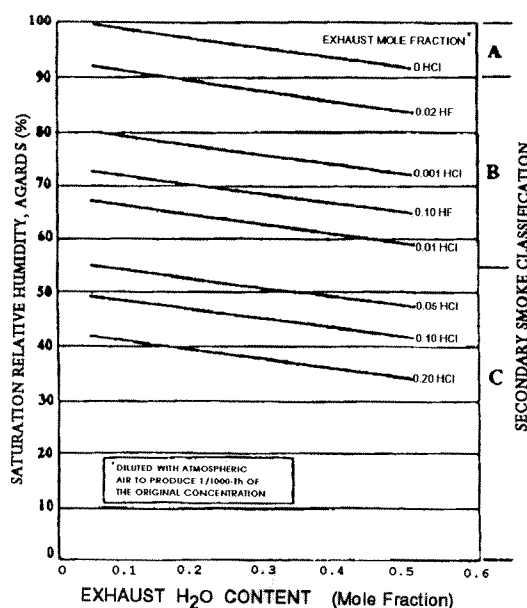


Figure 4.2.5.1-1 Saturation Relative Humidity for AGARD Secondary Smoke Classification at 0 °C, 1 atm.

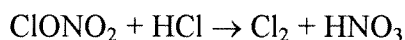
Modeling of the rocket exhaust effluent chemistry overall and local chemistry in the troposphere can be performed by the NASA/MSFC REED (Rocket Exhaust Effluent Diffusion) description (Refs. 4-24, 4-25, 4-26, 4-37, 4-40.) The data input requires local meteorological conditions; the program is not designed for the general case.

4.2.5.1.1 Ozone Reactive

The original emphasis, and still the main thrust for prevention of stratospheric ozone depletion is based on prevention of accumulation of tropospheric-stable, stratospheric-photo-decomposable chlorine and bromine species in the stratosphere. These originally included a number of CFCs (chlorofluorocarbons) used as aerosol propellants, foam plastic blowing agents, cleaning solvents, and refrigerants, some bromine analogs (Halon), and methyl chloroform. Later additions

have included HCFCs (hydrochlorofluorocarbons), and heavily chlorinated or brominated aliphatic hydrocarbons such as carbon tetrachloride, perchloroethylene, methyl bromide and bromoform.

Current understanding of the mechanisms for polar ozone depletion emphasizes the participation of nitric acid, HNO_3 , hydrogen chloride or hydrochloric acid, HCl , and ice crystals as necessary ingredients. Ice crystals that contain nitric acid trihydrate, $\text{HNO}_3 \cdot 3 \text{H}_2\text{O}$, (NAT), absorb a film of liquid HCl or its hydrate: molecules of chlorine nitrate, ClONO_2 , impinge on the film and react to form elemental chlorine and nitric acid;



As the mechanisms and the reaction sequences that affect ozone in the stratosphere have been more clearly elucidated, the various nitrogen, fine particles and droplets that serve as reaction sites have drawn attention. Both aerosol droplets of SO_2 and fine ice crystals are implicated. Artificial injection of any of the three into the stratosphere is considered undesirable.

Direct injection of other species that can form chlorine atoms under some circumstances, such as HCl and aluminum chloride hydrates, are under strong suspicion as ozone scavengers, and possible surface reaction on various metal oxide particles is currently an open question with many technologists, so their injection is unofficially classed as undesirable.

Absorption of HCl and water as a liquid (solution) from model exhaust onto calcined, powdered Al_2O_3 has been demonstrated in laboratory tests (Ref. 4-27) The product is postulated to contain dissolved alumina, and the projected soluble product is aluminum chloride hexahydrate.

Significant amounts of copper chloride derived from the copper-plated collectors were detected and semi-quantitatively analyzed by SEM from a dried acidic alumina aerosol droplet collected in the exhaust of Tomahawk TME-M-416 solid propellant motors fired at an out-of-doors test range at MFSC. Other extraneous metal salts, Fe, Ca, and Cr that were detected are artifacts of SEM procedures. No other metal salts were found by SEM analysis. The Al_2O_3 collected was a mixture of α and γ crystalline forms, with the latter predominating in the finest particles (Ref. 4-41) It is well-established that α alumina is non-reactive with HCl while γ reacts rapidly by dissolving as the soluble chloride.

4.2.5.1.1.1 Current Criteria; Standards; Sources

Proscribed species are officially ranked in ozone-destructive capability, the Ozone Depletion Potential (ODP). Only one species, Halon 2402, noted above as a rocket effluent, is contained in the list in Appendix A to EPA 40 CFR Part 82, Protection of Stratospheric Ozone Part II, published in the Federal Register, pp. 28094-228192, May 12, 1993. It is listed in Table 4.2.5-1.

Table 4.2.5-1 Proscribed ODP Species in Rocket Effluents

CFC Name & No.	Refrigerant No.	Chemical Name	Formula	ODP ^a	Phase out Date
Halon 2402	114B2	Dibromo tetrafluoro ethane	$\text{C}_2\text{F}_4\text{Br}_2$	6.2	Jan. 1, 1994

^a -- Relative to CFC-11 (CFCl_3).

The launches of current vehicles produce ozone-suspect species in their exhaust plumes. The quantities of some of these species projected for the Year 2000, see Tables 4.2.4-16 and -17 above, have been calculated and charted. The calculated sums of gaseous species ($\text{HCl} + \text{OH} + \text{Cl}$) and particulates ($\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$) from solid motor launches in the year 2000 are presented in Figures 4.2.5.1.1-1 and -2 below.

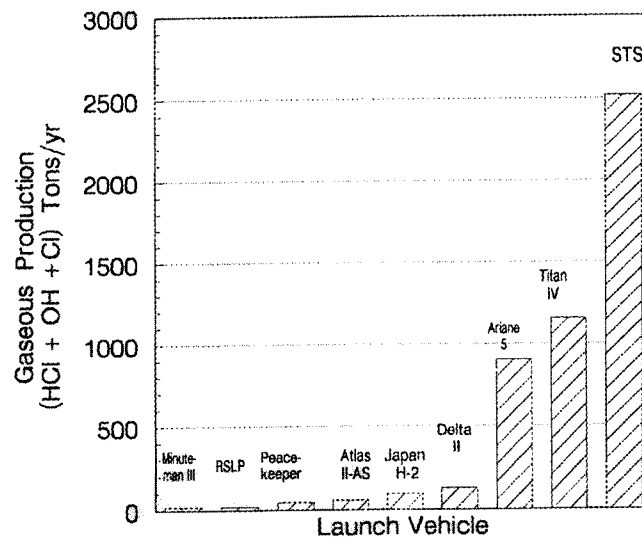


Figure 4.2.5.1.1-1 Exhaust Production of Suspect Gas Species From Current Solid Rocket Motors for Year 2000.

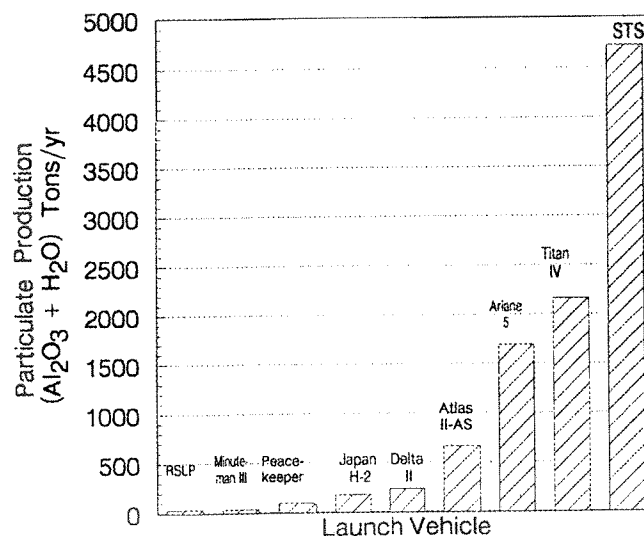


Figure 4.2.5.1.1-2 Exhaust Production of Particulate Species From Current Solid Rocket Motors for Year 2000.

4.2.5.1.1.2 Advanced Criteria; Standards; Sources

A number of chemical species that are not on the official proscription lists because of established ODP are suspected of causing or catalyzing ozone depletion when injected into the upper troposphere or stratosphere from the plume cloud. These are listed in Table 4.2.5-2.

HCl vapor is sometimes considered the sink that removes chlorine from the ozone depletion cycle, the HCl is then washed from the atmosphere. The photolysis of HCl to chlorine atoms has been demonstrated but the lifetime is ~a few days while Cl_2 produced by afterburning HCl in the plume participates promptly in the Rowland-Molina reaction cycle. UV photolysis of sodium chloride, NaCl, has been demonstrated (in the laboratory) to yield chlorine atoms. It is probable that many other chloride salts with similar or lower bond dissociation energies (100 kcal/mol, Ref. 4-42) will also.

The ice-surface reaction of nitrogen oxide with chlorine atoms has lead to the postulate, yet untested, that other solids, suspended as microparticles in the stratosphere, may provide similar catalytic surfaces. Currently, all such materials are suspect. Of course, metal chloride particulate is doubly suspect, as well as nucleation of ice on Al_2O_3 .

Vapors that condense to solids during high altitude plume expansion, as shown by contrails (condensation trails), may provide a surface for the chlorine-nitrogen oxide reaction, similar to the ozone depletion effect in polar springtime; these vapors include H_2O , CO_2 , and NH_3 .

Table 4.2.5-2 Potentially Restricted ODP Species in Plume Cloud

Species Formula	Exhaust Phase	Ozone Depletion Phase
H_2O	Vapor	Gas
N_2O	Vapor	
NO	Vapor	
NO_2	Vapor	HNO_3 solution
HCl	Vapor	Solution
NaCl	Solid	Solid
KCl	Solid	Solid
Al_2O_3	Solid	Solid
B_2O_3	Vapor/Solid	Solid
Fe_2O_3	Solid	Solid
CO_2	Vapor	Vapor
CH_4	Vapor	Vapor
$\text{M}_n\text{O}_{n/2}$	Solid	Solid
$(\text{C}_2\text{ClF}_3)_n$	Vapor	
Perfluoro hexane	C_6F_{14}	

Background trace gas concentrations affect the ODP of most ozone depleting species. Doubling the CH₄ concentration (1.6 → 3.2 ppm) increases CFC-12's ODP by 1%, doubling the CO₂ (340 → 600 ppm) increases it by 2%, a 20 % increase of N₂O (300 → 360 ppb) increases it by 5% (Ref. 4-43)

NOx emissions from ground installations are limited under Title I of the Clean Air Act, Ref. 4-36, because they participate in ozone formation, and under Title IV for Acid Rain, discussed in Section 4.2.5.1.3. The ozone-causing limits depend on plant size. Germany, the EC, and Japan impose limits based on plant size and fuel type, Ref. 4-44, Table 4.2.5-3.

Table 4.2.5-3 Foreign NOx Limits

Country	Fuel	Size	NOx Limit
Germany	Solid	>300 MW	200 mg/m ³ flue gas
	Liquid	>300 MW	150 mg/m ³ flue gas
	Gas	>300 MW	100 mg/m ³ flue gas
	Solid	100-300 MW	400 mg/m ³ flue gas
	Liquid	100-300 MW	300 mg/m ³ flue gas
	Gas	100-300 MW	200 mg/m ³ flue gas
Germany, 1995	Oil	>400 kW	150 mg/kW
	Gas	>400 kW	100 mg/kW
	Oil	70-400 kW	130 mg/kW
	Gas	70-400 kW	80 mg/kW
	Oil	<70 kW	110 mg/kW
	Gas	<70 kW	60 mg/kW
EC	Solid	--	650 mg/m ³ flue gas
	Liquid	--	450 mg/m ³ flue gas
	Gas	--	350 mg/m ³ flue gas
Japan	Coal	Small	480 ppm
	Gas	Large	60 ppm

4.2.5.1.1.2.1 Formation-Release Altitude

At this time, models of atmospheric convection/diffusion do not couple the migration of plume constituents downward from the mesosphere into the stratosphere.

4.2.5.1.1.3 Propellant Systems Implications

The Ozone Reactive species concentrations are rated for currently used propellants in Table 4.2.7-1, Summed System Environmental Evaluation. Concentrations of Ozone Reactive species in Ground and Plume Clouds for Advanced Propellants are listed below, in Table 4.2.5-4, in which the exhaust species concentrations are abstracted from Tables 4.2.4-1 to 4.2.4-4.

Table 4.2.5-4 Ozone Reactive Exhaust Constituents from Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Gas; Monopropellant			
H ₂	H ₂ ; 100	ANU	RCTD
		ANU	8.1 x 10 ⁻⁶
NH ₃	H ₂ ; 17.6	ANU	RCTD
	N ₂ ; 82.4	ANU	RCTD
	NOx;	ANU	
	Formed H ₂ O;	ANU	5.2 X 10 ⁻⁶
Li	Li; 100	ANU	RCTD
	Li ₂ O;	ANU	
	LiOH;	ANU	
Xe	Xe 100	ANU	NOR
Gas; Bipropellant			
H ₂ +O ₂ (ACS: MD/X Single-Stage to Orbit Subscale Test Vehicle)	H ₂ ; 3.4	NOR	RCTD
	H ₂ O; 96.6	NOR	
	NOx;		
	Total H ₂ O;	NOR	
Liquid; Monopropellant; Gelled			
Alumizine (Al-gelled hydrazine)	H ₂ ;	NOR	RCTD
	N ₂ ;	NOR	NOR
	NH ₃ ;	NOR	RCTD
	AlN;	NOR	POS
	Al ₂ O ₃ ;	NOR	POS
	NOx;		
	H ₂ O;	NOR	
	Total H ₂ O;	NOR	
Liquid; Bipropellant; Hypergolic			
LF ₂ + LH ₂	HF; 78.6	NOR	NOR
	H ₂ ; 0.3	RCTD	RCTD
	H; 0.1	RCTD	RCTD
	F; 20.1	RCTD	RCTD
	H ₂ O;	NOR	
	Total HF;	NOR	NOR
N ₂ H ₄ + N ₂ F ₄	HF; 57.6	NOR	NOR
	N ₂ ; 42.4	NOR	NOR
	NOx;		
N ₂ H ₄ + ClF ₅	HF; 54.8	NOR	NOR
	HCl; 21.0		
	N ₂ ; 24.2	NOR	NOR
	NOx;		
B ₂ H ₆ + OF ₂	H ₂ O; 14.7	NOR	
	HF; 31.0	NOR	NOR
	B ₂ O ₃ ; 19.0	NOR	POS
	BF ₃ ; 35.6	NOR	NOR
	NOx;		

Cont.

Table 4.2.5-4 (Cont.)
Ozone Reactive Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Liquid; Bipropellant; Hypergolic			
C ₂ H ₄ + OF ₂	HF;	67.8	NOR
	H ₂ O;	2.1	
	CO;	5.5	RCTD
	CO ₂ ;	5.9	NOR
	CF ₄ ;	18.8	NOR
	NOx; Total CO ₂ ;		
Liquid; Bipropellant; Gelled; Hypergolic			
F ₂ (gel) + N ₂ H ₄ (gel)	HF;	73.0	NOR
	N ₂ ;	26.9	NOR
	PF ₅ ;	0.03	
	CO;	0.03	RCTD
	CF ₄ ;	0.02	NOR
	NOx; CO ₂ ;		
Gel F ₂ + Gel H ₂	HF;	78.6	NOR
	H ₂ ;	0.3	RCTD
	H;	0.1	RCTD
	F;	21.0	RCTD
	CF ₄ ;	0.03	
	CO;	0.02	RCTD
	PF ₅ ;	0.03	NOR
	H ₂ O;		
	CO ₂ ; Total HF;		
Gel F ₂ + Gel NH ₃	HF;	80.2	NOR
	N ₂ ;	19.7	NOR
	PF ₅ ;	0.03	NOR
	CO;	0.03	RCTD
	CF ₄ ;	0.02	NOR
	NOx; Total CO ₂ ;		
N ₂ H ₄ + IRFNA (with gelling solids)	H ₂ ;		RCTD
	H ₂ O;		NOR
	Li ₂ O;		NOR
	CO;		RCTD
	CO ₂ ;		NOR
	SiO ₂ ;		NOR
	N ₂ ;		
	NOx;		
	Total CO ₂ ;		
	Total H ₂ O;		
	LiOH;		

Table 4.2.5-4 (Cont.)
Ozone Reactive Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/v	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Liquid; Bipropellant; Gelled; Hypergolic			
N ₂ H ₄ + IRFNA (with low smoke gelling solids)	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	N ₂ ;	NOR	NOR
	NOx;		
	Total CO ₂ ;		
	Total H ₂ O;		
Liquid-Slush			
H ₂ (slush) + LO ₂	H ₂ ; 3.4	RCTD	RCTD
	H ₂ O; 96.6	NOR	
	Total H ₂ O;		
Liquid-Solid Hybrid			
LO ₂ + Butyl rubber	H ₂ ; 1.0	RCTD	RCTD
	H ₂ O; 20.2	NOR	
	CO; 44.5	RCTD	RCTD
	CO ₂ ; 33.6	NOR	
	OH; 0.03	NOR	NOR
	N; 0.4	NOR	NOR
	Total CO ₂ ;		
	Total H ₂ O;		
Liquid-Solid Hybrid; Hypergolic			
LiBH ₄ + H ₂ O ₂	H ₂ ; 0.1	RCTD	RCTD
	H ₂ O; 76.8	NOR	NOR
	Li ₂ O; 5.9	NOR	POS RCTD
	B ₂ O ₃ ; 17.2	NOR	POS
	Total H ₂ O;		
	LiOH;		
Liquid; Tripropellant			
LO ₂ + [LH ₂ + CH ₄ / RP-1] (Ref.4-11)	H ₂ ; 0.1	RCTD	RCTD
	H ₂ O; 81.0	NOR	
	CO; 4.5	RCTD	RCTD
	CO ₂ ; 14.0	NOR	
	NOx;		
	Total CO ₂ ;		
	Total H ₂ O;		

Cont.

Table 4.2.5-4 (Cont.)
Ozone Reactive Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/v	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Solid; H, C, O, Cl Free			
NF ₄ BF ₄ + Li + Poly PNF ₂	PF ₅ ;	NOR	NOR RCTD
	BF ₃ ;	NOR	NOR
	N ₂ ;	NOR	NOR
	LiBF ₄ ;	NOR	POS
	NO _x ;	NOR	POS
	PN;	NOR	POS
	BN;		
	P ₂ O ₅ ;		
	HF;		
Solid; Cl-free exhaust			
GAP (Glycidyl Azide Polymer) + TMETN (Trimethylolethane trinitrate) + AN (NH ₄ NO ₃)	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;		
	Total H ₂ O;		
	Total CO ₂ ;		
Solid; HCl-free exhaust			
PGA + TEGDN + ZnO-Stabilized AN + MgAl	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;	NOR	POS
	MgO;	NOR	POS
	Al ₂ O ₃ ;		
HTPE + BuNENA + Amine phase-stabilized AN + MgAl	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;	NOR	POS
	MgO;	NOR	POS
	Al ₂ O ₃ ;		
	Total CO ₂ ;		
	Total H ₂ O;		

Table 4.2.5-4 (Cont.)
Ozone Reactive Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Solid; HCl-free exhaust			
HAN/AN + Al + PVA	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;		
	Al ₂ O ₃ ;	NOR	POS
	Total CO ₂ ; Total H ₂ O;		
Solid; Neutralized HCl			
HTPE + AN + AN + MgAl	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;	NOR	POS
	MgO;	NOR	POS
	Al ₂ O ₃ ;	NOR	POS
	MgCl ₂ ;		
	Total CO ₂ ; Total H ₂ O;		
Solid; Scavenged HCl			
HTPB + DOA + Al + NaNO ₃ + AP + 0.8% KP	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;		
	Al ₂ O ₃ ;	NOR	POS
	NaCl;	NOR	POS
	KCl;	NOR	POS
	Na ₂ O;	RCTD	RCTD
	K ₂ O;	RCTD	RCTD
	Total CO ₂ ;		
	Total H ₂ O;		
	NaOH; KOH;		

Cont.

Table 4.2.5-4 (Cont.)
Ozone Reactive Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Ground Cloud Ozone Reactive Species mg/m ³ of Cloud	50 km Plume Cloud Ozone Reactive Species mg/m ³ of Cloud
Solid; Scavenged HCl			
HTPB + AP + NaNO ₃ + HMX + Al	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	
	N ₂ ;	NOR	NOR
	NO _x ;		
	Al ₂ O ₃ ;	NOR	POS
	NaCl;	NOR	POS
	Na ₂ O;	RCTD	RCTD
	Total CO ₂ ;		
	Total H ₂ O;		
	NaOH;		
Solid; Decreased HCl			
AP, Al, CTPB, BITA, Polybutene, HAN, PVA	CO;	RCTD	RCTD
	CO ₂ ;	NOR	
	H ₂ ;	RCTD	RCTD
	H ₂ O;	NOR	NOR
	N ₂ ;	NOR	NOR
	NO _x ;		
	Al ₂ O ₃ ;	NOR	POS
	HCl; 2		
	Total CO ₂ ;		
	Total H ₂ O;		

ANU = Application Not Used

NOR = Not Ozone Reactive

POS = Possible Ozone Sensitivity

RCTD = Reacted

4.2.5.1.2 Global Warming/Greenhouse Effect

Reabsorption in the atmosphere of ground-emitted infrared radiation during its passage through the atmosphere (troposphere), instead of permitting it to escape from the Earth into space, affects the heat balance of the planet and is predicted to cause a gradual, world-encompassing temperature increase. The wavelength window of significance is 500 - 1400 cm⁻¹ (7.3 - 20 μm). The natural atmospheric constituents CO₂ and water vapor are the primary greenhouse gases. Actions of humankind produce an additional CO₂ burden, and the same chlorofluorocarbon compounds implicated in stratospheric ozone depletion also increase infrared absorption.

The mechanism of radiation re-adsorption depends on the absorption by the individual constituents of the atmospheric medium. The monoatomic noble gases helium, neon, argon, krypton and xenon, and the diatomic elemental gases oxygen, nitrogen, hydrogen and the halogens fluorine,

chlorine, bromine, and iodine are transparent in the infrared; almost all other gases and vapors, inorganic and organic, have infrared absorption bands. The absorption strength or intensity and exact wavelengths absorbed vary from species to species - thus the chemical analysis technique of infrared identification and quantitative determination. The effect of dusts and mists at lower altitudes is also to absorb terrestrially-emitted infrared. Compilations such as Satdler (Ref. 4-45) contain thousands of recorded infrared absorption spectra. Thus the great majority of plume-released species add to the warming burden.

4.2.5.1.2.1 Current Criteria; Standards; Sources

Global Warming Potential is defined as the ratio of steady-state infrared flux change calculated at the tropopause for each mass unit relative to the same for CFC-11.

4.2.5.1.2.2 Advanced Criteria; Standards; Sources

It is obvious that the presence of effluent species O_2 , N_2 , H_2 , and the elemental halogens in the expanded, equilibrated cloud need not be considered in evaluating global warming effects. But their initial presence must be evaluated in afterburning reactions that form infrared absorbent species, and only unreacted residues can be ignored.

4.2.5.1.2.3 Propellant Systems Implications

The Global Warming species concentrations are rated for currently used propellants in Table 4.2.7-1, Summed System Environmental Evaluation. Calculated quantities of Global Warming active species from current vehicles projected for the year 2000 from liquid propellants and solid propellants are charted in Figures 4.2.5.1.2-1 and -2.

Concentrations of Global Warming active species in Ground Clouds for Advanced Propellants are listed in Table 4.2.5-5 which follow the charts, in which the exhaust species concentrations are abstracted from Tables 4.2.4-1 to 4.2.4-4.

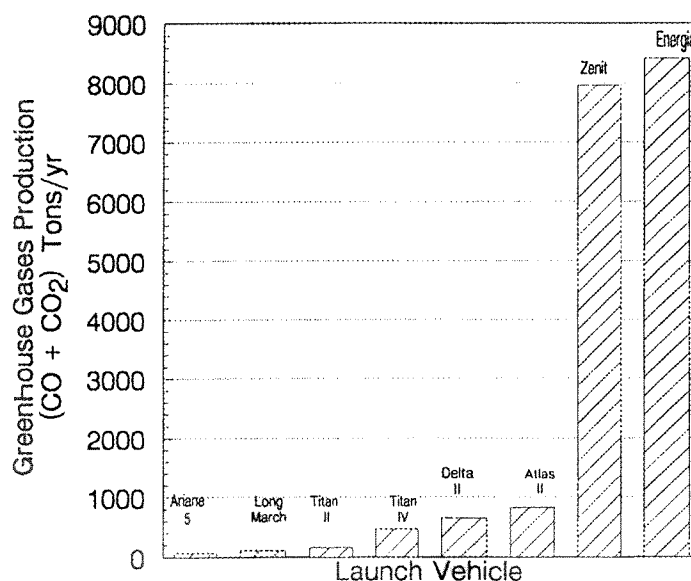


Figure 4.2.5.1.2-1 Exhaust Production of Greenhouse Gases from Liquid Rocket Engines Projected for Year 2000.

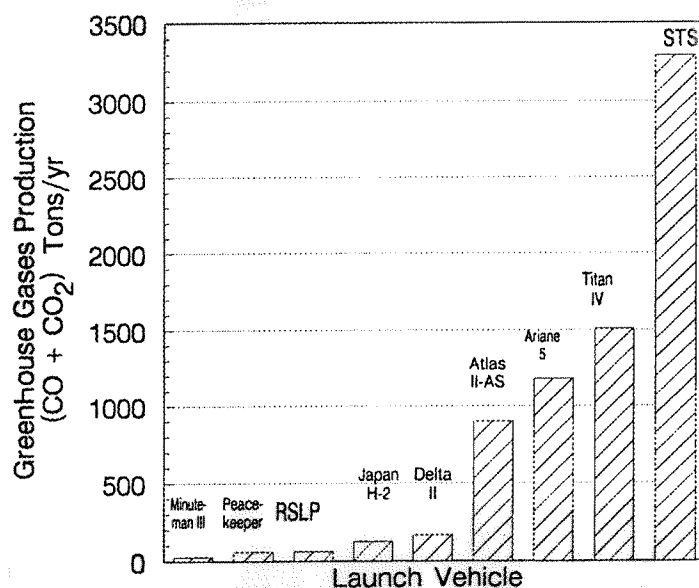


Figure 4.2.5.1.2-2 Exhaust Production of Greenhouse Gases from Solid Rocket Motors Projected for Year 2000.

Table 4.2.5-5 Global Warming-Active Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Exhaust Species Mass lb per Long Ton
Gas; Monopropellant		
H ₂	H ₂ ; 100	2240
NH ₃	H ₂ ; N ₂ ; NO _x ;	
Xe	Xe; 100	2240
Li	Li; 100	2240
Gas; Bipropellant		
H ₂ +O ₂ (ACS: MD/X Single-Stage to Orbit Subscale Test Vehicle)	H ₂ ; H ₂ O;	
Liquid; Monopropellant; Gelled		
Alumizine (Al-gelled hydrazine)	H ₂ ; N ₂ ; NH ₃ ; AlN; Al ₂ O ₃ ; NO _x ; H ₂ O;	

Table 4.2.5-5 (Cont.)
Global Warming-Active Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Exhaust Species Mass lb per Long Ton
Liquid; Bipropellant; Hypergolic		
N ₂ H ₄ + N ₂ F ₄	HF;	57.6
	N ₂ ;	42.4
	NO _x ;	
N ₂ H ₄ + ClF ₅	HF;	1290
	HCl;	950
	N ₂ ;	
	NO _x ;	
B ₂ H ₆ + OF ₂	H ₂ O;	1228
	HF;	470
	B ₂ O ₃ ;	542
	BF ₃ ;	
C ₂ H ₄ + OF ₂	H ₂ O;	329
	HF;	694
	CO;	426
	CO ₂ ;	797
	CF ₄ ;	
Liquid; Bipropellant; Gelled; Hypergolic		
F ₂ (gel) + N ₂ H ₄ (gel)	HF; N ₂ ; NO _x ; Metal F;	
Gel F ₂ + Gel H ₂	HF; Metal F;	
Gel F ₂ + Gel NH ₃	HF; N ₂ ; NO _x ; Metal F;	
N ₂ H ₄ + IRFNA (with gelling solids)	H ₂ ; H ₂ O; Li ₂ O; CO; CO ₂ ; SiO ₂ ; N ₂ ; NO _x ;	
Liquid-Slush		
H ₂ (slush) + LO ₂	H ₂ ;	76
	H ₂ O;	2164

Cont.

Table 4.2.5-5 (Cont.)
Global Warming-Active Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Exhaust Species Mass lb per Long Ton
Liquid-Solid Hybrid		
LO ₂ + Butyl rubber	H ₂ ;	22
	H ₂ O;	452
	CO;	997
	CO ₂ ;	753
	OH;	1
	N;	9
Liquid-Solid Hybrid; Hypergolic		
LiBH ₄ + H ₂ O ₂	H ₂ ;	
	H ₂ O;	
	Li ₂ O;	
	B ₂ O ₃ ;	
Liquid; Tripropellant		
LO ₂ + [LH ₂ + CH ₄ / RP-1] (Ref. 4-11)	H ₂ ;	2
	H ₂ O;	1814
	CO;	101
	CO ₂ ;	314
	NO _x ;	
Solid; H, C, O, Cl Free		
NF ₄ BF ₄ + Li or B + Poly PNF ₂	PF ₅ ;	
	BF ₃ ;	
	N ₂ ;	
	LiF;	
	NO _x ;	
	PN;	
Solid; Cl-free exhaust		
GAP (Glycidyl Azide Polymer) + TMETN (Trimethylolethane trinitrate) + AN (NH ₄ NO ₃)	H ₂ ;	
	H ₂ O;	
	CO;	
	CO ₂ ;	
	N ₂ ;	
	NO _x ;	
Solid; HCl-free exhaust		
PGA + TEGDN + ZnO-Stabilized AN + MgAl	CO;	
	CO ₂ ;	
	H ₂ ;	
	H ₂ O;	
	N ₂ ;	
	NO _x ;	
	MgO;	
	Al ₂ O ₃ ;	

Table 4.2.5-5 (Cont.)
Global Warming-Active Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Exhaust Species Mass lb per Long Ton
Solid; HCl-free exhaust		
HTPE + BuNENA + Amine phase-stabilized AN + MgAl	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; MgO; Al ₂ O ₃ ;	
HAN/AN + Al + PVA	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ;	
Solid; Neutralized HCl		
HTPE + AN + AN + MgAl	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; MgO; Al ₂ O ₃ ; MgCl ₂ ;	
HTPB + DOA + Al + NaNO ₃ + AP + 0.8% KP	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; NaCl; KCl; Na ₂ O; K ₂ O;	

Table 4.2.5-5 (Cont.)
Global Warming-Active Exhaust Constituents in Advanced Propellants

Propellant Constituents	Nominal Exhaust, % w/w	Exhaust Species Mass lb per Long Ton
Solid; Scavenged HCl		
HTPB + AP + NaNO ₃ + HMX + Al	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; NaCl; Na ₂ O;	
Solid; Decreased HCl		
AP, Al, CTPB, BITA, Polybutene, HAN, PVA	CO; CO ₂ ; H ₂ ; H ₂ O; N ₂ ; NO _x ; Al ₂ O ₃ ; HCl;	45
	2	

4.2.5.1.3. Acid Rain

Water-soluble gases and vapors in the atmosphere are dissolved by raindrops and make them acidic (pH < 7). When the drops fall to the ground they are acid rain. This process occurs with natural lightning-caused NO_x and is the major natural source of fertilizer nitrogen for non-leguminous plants. It also takes place to remove HF, HCl, and SO₂ from volcanoes. However, when human activities add acidic species to the atmosphere, the acid rain formed can overpower natural process and kill plants and water biota, and severely corrode stone artifacts.

4.2.5.1.3.1 Current Criteria; Standards; Sources

Unfortunately, current standards and criteria for acid rain maxima control the acidity (pH) of the collected rainfall, not the airborne content of acidic species. It is necessary to apply chemical theory, including vapor pressure relations, solubility relations, gas transport kinetics, and chemical kinetic theory to relate the atmospheric composition to the observed rainfall acidity.

The Clean Air Act, Title IV, Ref. 4-36 limits NO_x, but only from coal burning utility sources. As of Jan. 1, 1995, the limits will be 0.45 lb NO_x/million BTU from tangential fired boilers, and 0.50 lb NO_x/million BTU from wall fired boilers.

4.2.5.1.3.2 Advanced Criteria; Standards; Sources

Acid rain formation is not a consideration at stratospheric altitudes. It can be significant in the plume cloud above the troposphere.

4.2.5.2 Safety

sources: OSHA, CAL-OSHA, NIOSH, NFPA

MPSE (Missile Propellant Safety Evaluation) Program, Ref. 4-46
SOPHY (Solid Propellants Hazards Program), Ref. 4-47

Project PYRO, a study of "Liquid Propellant Explosive Hazards", Ref. 4-48, includes the cryogenic system $\text{LO}_2 + \text{LH}_2$, the semi-cryogenic system $\text{LO}_2 + \text{RP-1}$, and the storable hypergolic system $\text{N}_2\text{O}_4 + \text{Aerzine-50}$ (50% N_2H_4 /50% UDMH). Tests were conducted of explosions resulting from mixing (with ignition, if necessary) the propellants in conditions representing 1). a common bulkhead failure on the vehicle; 2). a launch failure vehicle fallback onto a launch pad resulting in one surface confinement by the ground surface; and 3). high velocity impact. Numerous measurements were collected, and a complicated method, a mixture of graphical interpolations and algebraic calculations, for predicting blast over pressure and heat transfer effects was developed, see volume 3, "*Prediction Methods.*", of the reference. It is not known whether this method has ever been reduced to a computer model, no such approach could be found by a literature survey or through CPIA. The graphical model approach has been applied (Ref. 4-49) for over pressure prediction.

Reviews of the documents, CPIA Manual, "*Chemical Rocket-Propellant Hazards.*", (Ref. 4-50), CPIA Manual, "*Hazards of Chemical Rockets and Propellants.*", (Ref. 4-51), HEPS (High Energy Propellant Safety) Program, (Ref. 4-52), and SPHAM (Space Propulsion Hazards Analysis Manual), (Ref. 4-53), resulted in the conclusion that current safety evaluations are highly launch system specific. No general figures of merit, to facilitate intersystem comparisons, are presented.

The CPIA Manual, "*Chemical Rocket-Propellant Hazards.*" states that it "is intended as a source of information and as a set of basic guidelines for the handling, storage, and transportation of liquid chemical propellants and propellant ingredients." It does not address the application systems to any great degree.

The CPIA Manual, "*Hazards of Chemical Rockets and Propellants.*" provides a set of guidelines for processing, handling, storage, and transportation of chemical rocket and gun propellants, and their ingredients. It provides quantity-distance requirements for liquid and solid propellant ingredients and systems.

The HEPS report states that its objective was "to determine the fundamental factors important to the safe deployment of large solid rocket motors loaded with energetic propellants. These studies focused on ... deflagration, detonation, shock-to-detonation, and deflagration-to-detonation transition of explosives and rocket propellants." It emphasizes what mechanisms initiate various hazardous effects, and does not evaluate system risks.

The SPHAM manual does not address specific systems; it presents a detailed how-it-must-be-done methodology for evaluating vehicle system hazards and risk assessment, with 457 references. Of course, hazards and risks associated with the propellant system are included.

For this document, the decision has been made that two safety/hazard aspects of the propulsion system as a whole are to be addressed. The first is the general on-pad hazard of an installed, ready to go flight system, as it affects personnel who are not assigned/occupied in the immediate vicinity -- this figure of merit is based on the established quantity-distance requirements

for current in-use systems, and on calculated peak over pressure from 100 klb of advanced propellants (see Section 4.2.5.2.3.) The second is for the transportation safety of the vehicle system, which is evaluated here only for solid propellant systems - it is assumed that liquid propellant systems are charged on the launch pad. The figure of merit is related to ease of ignition, and the explosive category.

The exhausts from expended propellant are wastes, and may contain hazardous constituents. However they do not meet the usual criteria to be officially classified as "Hazardous Waste." The safety requirements for hazardous wastes, that largely deal with their storage and transportation, are recorded in the federal government documents that contain the body of regulations listed below.

Department of Transportation	49 CFR Subtitle B Parts 100-199 Hazmat HM-181 Parts 800-899, 1000-1399
Environmental Protection Agency	40 CFR Parts 1-799 Air 1-99 Water 100-149, 400-699 RCRA 190-299 TSCA 700-end
Labor/Occupational Safety and Health Administration	29 CFR Parts 1900-1999 Gen. Ind. Std. 1900-1910.1000
National Institute of Standards and Technology	14 CFR Parts 200-299
Food and Drugs	21 CFR Parts 100-end

These are not the only applicable rules, but they do contain the greatest part of them.

Regulations of the Bureau of Mines, in 30 CFR, the Bureau of Alcohol, Tobacco Products and Firearms, 27 CFR and the Federal Aviation Administration, 14 CFR Parts 1-199, and the Coast Guard, 46 CFR Parts 1-199, must often be complied with for specific hazardous materials, sources or other situations.

A very significant Revision to 49 CFR Parts 107, "Hazardous Materials Program Procedures.", and Parts 171 through 180 on Hazardous Materials Transportation was published in 1990. The federal listing of specific hazardous substances is recorded the Appendix to Sec. 172.101.

4.2.5.2.1 Toxicity

4.2.5.2.1.1 Current Criteria; Standards; Sources

There are a number of agencies that regulate upper concentration limits for toxic species; the agencies include OSHA, EPA, CAL-OSHA, and others. In addition, other organizations develop upper exposure limits that are frequently cited by the regulatory agencies. The following data, Table 4.2.5-6, were abstracted from Reference 4-54, an OSHA-published handbook.

Table 4.2.5-6 Toxicity Ratings of Rocket Exhaust Species (Ref. 4-54)

Species	NFPA Rating			Toxicity Hazard Rating	OSHA PEL		ACGIH/TLV		NIOSH REL		Immed Dangr
	F	H	R		TWA	STEL	TWA	STEL	TWA	STEL	
	Rating				mg/m ³		mg/m ³		mg/m ³		ppm
Vapors											
Ammonia NH ₃	1	3	0	Skin 3-2 Eyes 3-2 Mucosa 3-2 Ingest 3-2 Inhale 3-2	--	27.0	18.0	27.0	--	35.0 5 min	500
Boron tri-fluoride BF ₃	0	3	1	Skin 3-2 Eyes 3-2 Mucosa 3-2 Ingest 3-2 Inhale 3-2	--	3 Ceilin g	--	3 Ceilin g	--	--	100
Carbon dioxide CO ₂	--	--	--	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	18000	54000	9000	54000	18000	54,000 10 min	50,000
Carbon monoxide CO	4	2	0	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	40	229	55	440	35 PPM	200 PPM	1500
Chlorine Cl ₂	0	3	0	Irritant 3 Inhale 3	1.5	3.0	3.0	9.0	--	1.5 15 min	30

Cont.

**Table 4.2.5-6 (Cont.)
Toxicity Ratings of Rocket Exhaust Species (Ref. 4-54)**

Species	NFPA Rating			Toxicity Hazard Rating	OSHA PEL		ACGIH/TLV		NIOSH REL		Immed Dangr ppm
	F	H	R		TWA	STEL	TWA	STEL	TWA	STEL	
					mg/m ³		mg/m ³		mg/m ³		
Vapors (Cont.)											
<i>unsymet</i> Dimethyl hydrazine (CH ₃) ₂ N ₂ H ₂	3	3	1	Suspect <u>carcinogen</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	1.0	--	1.0	--	--	0.15 20 min	--
Hydrazine N ₂ H ₄	3	3	3	<u>Carcinogen</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	0.1	--	0.1	--	--	0.04 120 min	--
Hydrogen chloride HCl	0	3	0	--	7.0 Ceiling		7.0 Ceiling		--	--	100
Hydrogen fluoride HF	0	4	0	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	3.0 ppm	6.0 ppm	2.5 ceiling g	2.5	5.0 15 min	30	
Hydrogen sulfide H ₂ S	4	3	0	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	14	21	14	21	--	15 10 min	300
Methyl hydrazine CH ₃ N ₂ H ₃	3	3	2	Suspect <u>carcinogen</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	0.35	--	0.35	--	--	0.08 120 min	--
Nitric oxide NO	--	--	--	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	30	--	30	--	30	--	100

Cont.

Table 4.2.5-6 (Cont.)
Toxicity Ratings of Rocket Exhaust Species (Ref. 4-54)

Species	NFPA Rating			Toxicity Hazard Rating	OSHA PEL		ACGIH/TLV		NIOSH REL		Immed
	F	H	R		TWA	STEL	TWA	STEL	TWA	STEL	Dangr
					mg/m³		mg/m³		mg/m³		ppm
Vapors (Cont.)											
Nitrogen dioxide NO ₂	--	--	--	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	--	1.8	6.0	10.0	--	1.8 15 min	50
Sulfur dioxide SO ₂	0	3	0	Irritant 3 Ingest 3 Inhale 3	5	10	5	10	1.3	--	100
Mists											
Ammonium hydroxide NH ₄ OH	Not separately rated; see Ammonia vapor										
Hydro-chloric acid HCl.nH ₂ O	Not separately rated; see Hydrogen chloride										
Nitric acid HNO ₃	0	3	0	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	5.0	10.0	5.0	10.0	5.0	--	100
Nitrous acid HNO ₂	Not rated										
Sulfurous Acid = SO ₂ Aerosol	Not separately rated; see Sulfur dioxide										
Sulfuric Acid H ₂ SO ₄	0	3	2	Skin 3-2 Eyes 3-2 Mucosa 3-2 Ingest 3-2 Inhale 3-2	--	1.0	--	1.0	--	1.0	80 mg/m³
Particles											
Aluminum oxide Al ₂ O ₃	0	1	1	Causes Shaver's disease Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	5	--	10	--	--	--	--

Cont.

**Table 4.2.5-6 (Cont.)
Toxicity Ratings of Rocket Exhaust Species (Ref. 4-54)**

Species	NFPA Rating			Toxicity Hazard Rating	OSHA PEL		ACGIH/TLV		NIOSH REL		Immed Dangr	
	F	H	R		TWA	STEL	TWA	STEL	TWA	STEL		
					mg/m³		mg/m³		mg/m³			
Particles												
Ammonium chloride; fume NH ₄ Cl	0	1	0	Skin 3-2 Eyes 3-2 Mucosa 3-2 Ingest 3-2 Inhale 3-2	10.0	20.0	10.0	20.0	--	--	--	
Boron oxide B ₂ O ₃	--	--	--	Ingest 3	10	--	10	--	--	--	--	
Carbon dust C	--	--	--	Suspect carcinogen	3.5	--	3.5	--	3.5	--	--	
Iron oxide dust Fe ₂ O ₃	--	--	--	Causes <u>siderosis</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	10	--	5	--	--	--	--	
Lead dust or fume Pb	--	--	--	Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	--	0.05	--	0.15	--	0.1	--	
Silica dust crystal: crista-bolite; quartz SiO ₂	--	--	--	Causes <u>silicosis</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	--	0.1	--	0.1	--	0.05	--	
Silica dust crystal: tridymite SiO ₂	--	--	--	Causes <u>silicosis</u> Skin 3 Eyes 3 Mucosa 3 Ingest 3 Inhale 3	--	0.05	--	0.05	--	0.05	--	

Cont.

**Table 4.2.5-6 (Cont.)
Toxicity Ratings of Rocket Exhaust Species (Ref. 4-54)**

Table notes:

OSHA PEL = Occupational Safety and Health Agency Permissible Exposure Level.

NFPA Rating = National Fire Protection Association Rating; F = Flammability, H = Health, R = Reactivity;
0 = none, 1 = slight, 2 = moderate, 3 = severe, 4 = extreme.

ACGIH/TLV = American Council General for Industrial Health Threshold Limit Value.

NIOSH REL = National Institute for Occupational Safety and Health Recommended Exposure Limit.

TWA = Time Weighted Average.

STEL = Short Time Exposure Limit.

Toxicity Hazard Rating; 1 = Low, 2 = Moderate, 3 = High; (Ref. 4-55)

The following toxic chemicals release limits, Table 4.2.5-7, were abstracted from the Table II of the EPA Toxic Chemical Release Inventory Section 313 (Ref. 4-56).

Table 4.2.5-7 EPA Reporting Limits for Toxic Chemicals Release

Species	Formula	De Minimis Concentration % w/w
Vapors		
Ammonia	NH ₃	1.0
Chlorine	Cl ₂	1.0
1,1-Dimethyl hydrazine	(CH ₃) ₂ N ₂ H ₂	0.1
Hydrazine	N ₂ H ₄	0.1
Hydrochloric acid	HCl	1.0
Hydrogen fluoride	HF	1.0
Methyl hydrazine	CH ₃ N ₂ H ₃	1.0
Mists		
Ammonium hydroxide	NH ₄ OH	1.0
Nitric acid	HNO ₃	1.0
Dusts/Fumes		
Lead	Pb	0.1

Note that in this federal requirement, SIC code 37: Transportation Equipment, includes subcodes 3761 Guided missiles and space vehicles; 3764 Guided missile and space vehicle propulsion units and propulsion unit parts; and 3769 Guided missile and space vehicle parts and auxiliary equipment. If employees at a subcode facility number more than 11, and more than 10,000 lb. per year of any of the chemicals in Table 4.2.5-7 are released (e.g., as rocket exhaust) from that facility at concentrations above the De Minimis values, an EPA Form R may have to be submitted.

The EPA concentration limits, in Table 4.2.5-7, are far above the OSHA hazardous toxicity rating limits listed in Table 4.2.5-6 and are not further considered for this document.

4.2.5.2.1.2 Implications

Adopting the usual STEL PEL concentration of mg/m^3 as used for toxicity limit standards, the concentration for a single toxic species from firing a vehicle that employs an individual propellant can be estimated by the calculation

$$\text{Toxic wt, T} \times 2240, \text{ lb./T} \times 453, \text{ g/lb} \times 1000, \text{ mg/g}$$

$$\Sigma (\text{gas wt}), \text{ T} \times 2240, \text{ lb./T} \times 453, \text{ g/lb} \times 20.37 \text{ g.mol/g} \times 22.4 \text{ L/mol} \times 0.001 \text{ m}^3/\text{L}$$

The weight of solids in the exhaust products is excluded from the volume calculation in the denominator. This calculation is based on an average molecular weight for gas and vapor products of 20.37 g/g.mol . The assumptions are no mixing of exhaust with surrounding air, and an ambient exhaust temperature, so there are no temperature corrections. Condensation of vapors to liquid, mostly as droplets, and absorption of vapors onto solid particles is ignored. The above simplifies to:

$$\text{Toxic Conc., mg/m}^3 = \frac{\text{weight of toxic species(tons)} \times 2.192 \times 10^3}{\text{sum of weights of gases and vapors (tons)}}$$

A linear rating scale is selected that is open ended, starting at 0, and values greater than 1 indicate hazardous concentrations. Values between 0 and 1 indicate the fraction of hazardous material relative to the OSHA limit; values greater than 1 indicate the actual concentration as a multiple of the hazard limit.

$$R_T = \text{Toxicity rating} = \left(\frac{\text{Toxic Conc.}}{\text{OSHA/PEL STEL}} \right)$$

The calculated Toxicity Ratings for currently used propellants are included in Table 4.2.6-1, Summed System Safety Evaluation.

4.2.5.2.2 Odor Control

The 1990 Clean Air Act Amendments (CAAA), Ref. 4-36 under the National Emissions Standards for Hazardous Air Pollutants (NESHAPs), Ref. 4-57, regulate specific odor-causing chemicals, Ref. 4-58. The following table, 4.2.5-8, lists many of the species and their typical lower detection limits by the human sense of smell. The table includes only a few propellant combustion products, but it serves as a warning of potential additional limits.

Table 4.2.5-8 Common Odor-Causing Compounds

(Unregulated Items Noted. Ref. 4-58)

Compound	Odor	Odor Threshold
	Description	ppb
Chlorophenol UR	Medicinal	0.18
Ethyl sulfide	Ethereal	0.25
Hydrogen sulfide UR	Rotten eggs	0.4
Dimethyl sulfide UR	Garlic	1.0
Ethyl mercaptan UR	Leek-like	1.0
Methyl mercaptan UR	Decayed cabbage	1.1
Skatole UR	Fecal	1.2
Nitrobenzene	Almond	4.7
Phosphine	Decaying fish	21
Benzyl chloride	Irritating	47
Phenol	Medicinal	47
Styrene	Penetrating	47
Acetaldehyde	Pungent	210
Acrolein	Pungent	210
Carbon disulfide	Decay	210
Methyl methacrylate	Acrid	210
Chlorine	Suffocating	310
Sulfur dioxide UR	Pungent	470
Allyl chloride	Pungent	470
Methyl isobutyl ketone	Camphor	470
Formaldehyde	Pungent	1,000
Phosgene	Suffocating	1,000
Toluene di-isocyanate	Pungent	2,140
Perchloroethylene	Ethereal	4,680
Hydrochloric acid	Pungent	10,000

UR = Unregulated under NESHAPs.

Odor thresholds do not necessarily correspond with emissions limits in CAAA.

4.2.5.2.3 Storage

4.2.5.2.3.1 Current Criteria; Standards; Sources

Storage of propellant-loaded launch vehicles, for the purposes of this report that is directed at issues from combustion exhaust, is considered to be during the pre-ignition period on/in the launch facility. Usually, liquid propellants are not loaded into vehicles before they are installed at the facility; solid propelled vehicles are transported to the facility fully loaded, and placed therein in a ready to operate condition.

Because a non system-specific storage hazard rating scale does not seem to be in common use, one has been selected for this project in order to enable comparative ratings. It is based on the commonly used Quantity-Distance requirements. There are actually two related scales. One, for fully characterized flight systems, is termed the PQD scale, and is the base ten logarithm of the separation distance (in feet) for the selected vehicle fully loaded with propellant. The other, for propellant or propulsion system development, is named PDP, and is the base ten logarithm of the radius for 0.25 psi over pressure from the most rapid combustion of 1 ton of premixed propellant or

accident-mixed ingredients. The logarithms are used to obtain number values that are easy to compare.

4.2.6 Ratings of Propellant Systems

Table 4.2.6-1 Systems Safety Evaluation

Propellant System	Devlpmnt Status	Insensitive Munitions Ratings	Toxicity Ratings
Atlas II (USA) LH ₂ +L O ₂	In Use	--	CO; 3.1 CO ₂ ; 0.011
Atlas II, AS (USA) LH ₂ +L O ₂ with Strap Ons	In Use	--	CO; 3.1 CO ₂ ; 0.0097 HCl; 11 Al ₂ O ₃ ; 22
STS(USA) LH ₂ +L O ₂ with Strap Ons	In Use	--	CO; 1.3 CO ₂ ; 0.0010 HCl; 49 Al ₂ O ₃ ; 98
Delta(USA) LH ₂ +L O ₂ with Strap Ons	In Use	--	CO; 3.7 CO ₂ ; 0.0094 HCl; 30 Al ₂ O ₃ ; 60
Titan II (USA) MMH+ N ₂ O ₄	In Use	--	CO; 0.5 CO ₂ ; 0.007
Titan IV (USA) MMH+ N ₂ O ₄ with Strap Ons	In Use	--	CO; 2.3 CO ₂ ; 0.0037 HCl; 61.6 Al ₂ O ₃ ; 8.6

Cont.

**Table 4.2.6-1 (Cont.)
Summed Systems Safety Evaluation**

Propellant System	Devlpmnt Status	Insensitive Munitions Ratings	Toxicity Ratings
Minuteman (USA) Solid	In Use	--	CO; 2.6 CO ₂ ; 0.0058 HCl; 93 Al ₂ O ₃ ; 186
Peacekeeper (USA) Solid	In Use	--	CO; 3.6 CO ₂ ; 0.0013 HCl; 95 Al ₂ O ₃ ; 249
RSLP (USA)	In Use	--	CO; 1.9 CO ₂ ; 0.013 HCl; 54 Al ₂ O ₃ ; 71 Pb; 100 H ₂ S; 0.63
Ariane 5 Europe	In Use	--	CO; 3.05 CO ₂ ; 0.0025 HCl; 51.7 Al ₂ O ₃ ; 159
Energia (CIS)	In Use	--	CO; 2.45 CO ₂ ; 0.0072
Zenit (CIS)	In Use	--	CO; 7.3 CO ₂ ; 0.021
Long March (China)	In Use	--	CO; 0.60 CO ₂ ; 0.0079
H-2 (Japan)	In Use	--	CO; 2.31 CO ₂ ; 0.0014 HCl; 66 Al ₂ O ₃ ; 123

5.0 Conclusion and Recommendations

5.1 Conclusions

A methodology for the systematic removal of PORC from rocket plume exhaust streams using alternate propellants has been presented. The launch system impacts range from a minimum of a reformulated conventional solid propellant containing ammonium perchlorate but with afterburning suppressant chemicals added, to a completely reformulated solid propellant incorporating nitrate/carbonate oxidizers, to new or redeveloped engines burning conventional liquid propellants, and in the case of maximum launch system impact, a new launch system with engines based on fluorine oxidizers. This methodology can be implemented in stages depending on the level of PORC removal desired. That is, reformulated solids with afterburning suppressants can be implemented as a direct response to Cl_2 production, conventional liquid engines utilizing LOX/ LH_2 and/or LOX/RP-1 can be implemented to remove HCl and fluorine systems (solids and/or gels) can be implemented to eliminate H_2O and CO_2 (if greenhouse gases are a concern). All of the technologies and propellants discussed here have some level of demonstrated development.

The technology status of alternate propellants associated with the removal of PORCs has been reviewed. Afterburning suppressant chemicals have been identified which can be used to reformulate conventional AP based solid propellants. New solid propellant formulations based on nitrates and/or carbonates have been developed under USAF sponsorship but the lower specific impulse of such systems makes them unattractive for boost to LEO applications. Rocket engine technology utilizing conventional liquids as alternate propellants such as LOX/ LH_2 and/or LOX/RP-1 is well developed, have acceptable Isp values and are flight demonstrated, but this technology is not in current use in this country for heavy lift boost applications. NASA engine development programs focusing low cost boost to LEO engines provide directly applicable technology solutions to ozone depletion mitigation. Conventional liquid propellant launch systems represent the best near term solution to the PORC problem if reformulated solid propellants are unacceptable. This assumes that the ozone depletion due to heterogeneous reactions due to water condensation is acceptable. The status of fluorine based oxidizer rocket engine technology has been briefly reviewed. While liquid fluorine rocket engines have been developed and tested it is unlikely such engines would be flown in boost to LEO applications. Should fluorine oxidizer launch systems be developed it will very likely be as solid or gelled systems. There is sufficient technology available which suggests that solid propellants based on fluorine oxidizers could be produced at thrust levels supporting boost applications. Gelled propellant technology applied to fluorine oxidizers has not been demonstrated. Hybrid engine technology based on a liquid fuel, i.e. LH_2 , slush H_2 , liquid N_2H_4 with solid fluorine based oxidizer is credible, but has not been developed.

Results of calculations have been presented comparing the ozone depletion of conventional solid propellants with that of alternate propellants LOX/ LH_2 and LOX/RP-1. These calculations demonstrate that the liquid bipropellants provide much reduced ozone depletion. Arguments are presented which suggest that fluorine based propulsion systems may be even more benign with respect to ozone depletion.

A summary of the safety, performance characteristics and atmospheric environmental interactions for several existing and potential propulsion systems is presented. Propulsion and

propellant systems are described in terms of their environmental characteristics with respect to ozone depletion, greenhouse gas production and acid rain potential. Safety characteristics are evaluated and include toxicity storage and handling and propellant sensitivity.

5.2 Recommendations

Several recommendations can be made based on the discussions presented in this report. Given that afterburning suppression to prevent Cl_2 formation may be an acceptable near term solution to PORC production, a series of lab/bench/test stand tests are necessary to identify and demonstrate that afterburning suppressant chemicals which can be used as additives to supplement existing solid propellant formulations. At the laboratory or bench scale, potential suppressant chemical additives can be tested in either simulated plume/atmosphere shear layers or bombs to quantify afterburning suppression efficiency. Optical diagnostics can be used to probe the exhaust plume for HCl to Cl_2 conversion. When potential afterburning chemicals are identified, candidate solid propellant with suppressants should be formulated and test stand fired while probing the plume for HCl to Cl_2 reactions. Several of these motors should be flight dropped and similar measurements made at altitude.

Figure 5.2–1 depicts the essential features of the test. A supersonic flow representing the rocket exhaust stream is created. The conditions of pressure, temperature, Mach number and species mole fractions at the nozzle exit plane are representative of those found in boost-to-LEO systems. The entire nozzle exit plane is not simulated, only the fraction that participates in the shear layer afterburning. The second stream shown in the sketch is simulated atmosphere at stratospheric conditions of pressure, temperature and composition. Initially, it may be of interest to have pressure matched shear layers to simplify the gas dynamic interaction between the two streams. The rocket exhaust stream temperature and composition can be altered to simulate different propellants at different O/F ratios with and without afterburning chemicals. The high speed shear layer is monitored with optical diagnostics, monitoring species indicative of afterburning such as OH and H_2O . The efficiency of candidate afterburning suppression chemicals can be quantified under representative conditions.

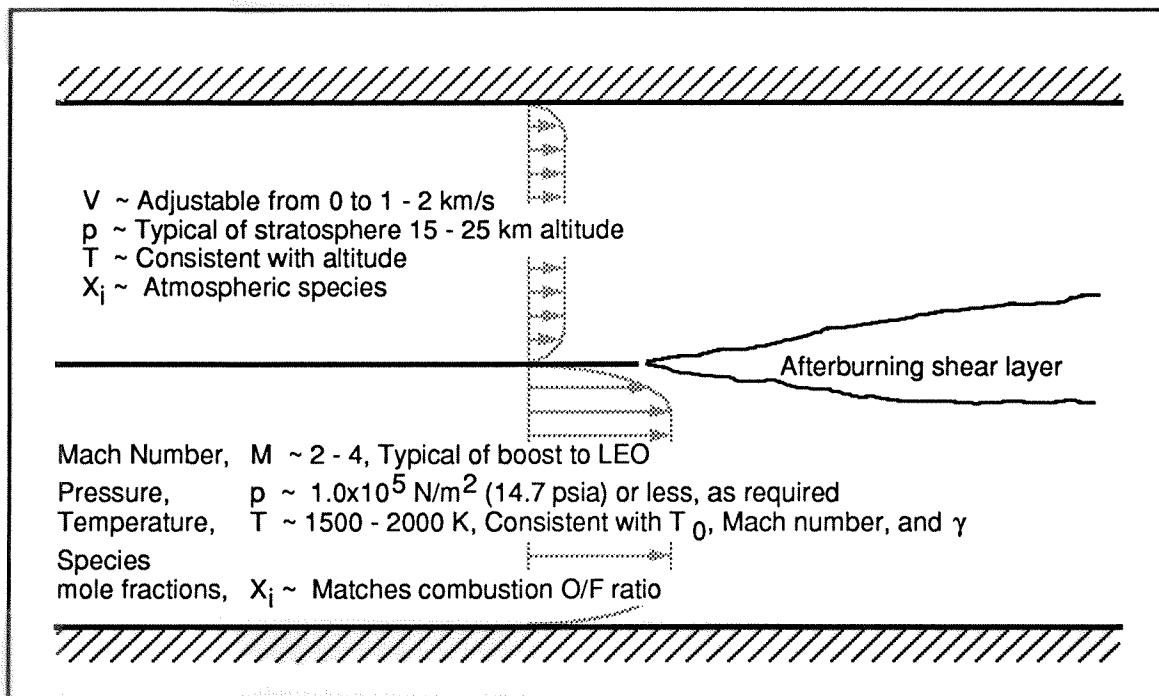


Figure 5.2-1 Sketch of Supersonic Plume/Atmospheric Shear Layer for Identification of Afterburning Suppression Propellant Additives

It appears that an increased understanding of heterogeneous nucleation processes related to the heterogeneous ozone depletion chemistry is warranted. This phenomena makes conventional liquid propellants, which typically produce significant amounts of water, either acceptable or unacceptable as environmentally sensitive propellants

The modeling of the short term, i.e. 0-3 days, plume/atmosphere ozone depletion chemistry also requires further development. Incorporation of multiple nozzle effects on the flowfield temperature, velocity and species distributions is essential since the individual exhaust plume interactions influence the afterburning regions. Different type of models, 1-D, 2-D, and 3-D should be developed so as to obtain consistency of results. Given that different boosters have different configurations, booster specific calculations should be performed to quantify the ozone depletion potential for each type of booster. These results can be used to make more accurate estimates of stratospheric ozone depletion and recovery.

Fluorine based solid and gelled propellants appear promising for several reasons. The promise of high Isp is always attractive in chemical propulsion. Propulsion system designers have been aware for years of the performance potential of liquid fluorine oxidizers. Materials compatibility, safety and handling issues have prevented fluorine oxidizers from being routinely used as propulsion systems. Solid and gelled propellants are acceptable from safety and handling perspectives which liquid fluorine is not. It appears worthwhile to develop fluorine propellants as either solids, gels or hybrids to exploit the performance potential of fluorine with acceptable handling and safety characteristics

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